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Mechanochemical Grinding of Industrial Mineral Fillers for Department of Supply and Services Canada

EXECUTIVE SUMMARY

A contract from the Department of Supply and Services Canada was awarded to the Ontario Research Foundation to investigate the technical feasibility of chemically modifying the surface of industrial mineral fillers during the grinding stage. The purpose of this study was to substitute relative expensive conventional organic surface modifiers by inexpensive organic solvents at lower consumption rates. The implementation of this technique could help the Canadian Mineral Industry to gain a bigger market share in the field of value added mineral, plastic fillers.

The chosen minerals for the conducted test work were calcite and talc from Ontario, suzorite mica from Quebec and silica from Manitoba. Propionic acid, isopropanol, di-isopropyl ether, methyl isopropyl ketone and kerosene served as alternative organic solvents which were added to the grinding stage. As an indicator for the dispersion behaviour of the mineral filler in plastic resins, the (surface related) oil adsorption test was used as suggested by ASTM standards (D 281 & D 1755).

It was found that surface hydration of the minerals inhibits their surface modification during wet grinding. However, significantly improved surface properties were achieved with all tested minerals by dry grinding with organic solvent additions which were threefold lower than for conventional surface modifiers. The best performing mineral additive combinations in the order of increasing improvements were: silica - propanol, suzorite - propionic acid, talc - propionic acid and calcite - propionic acid. From desorption tests it was concluded that, in most cases, the surface modification was based on the formation of organic solvent layers, which are chemically bonded to the mineral surfaces. The best surface modified calcite and talc products from the undertaken test work were found to be comparable to comprehensive commercial surface modified fillers.

Further pilot plant studies in connection with industrial partners as well as fundamental research are recommended.

1. INTRODUCTION

The Ontario Research Foundation was awarded a contract from the Department of Supply and Services Canada to investigate the technical feasibility of chemically modifying the surface of industrial mineral fillers during the grinding stage. The contract titled "Mechanochemical Grinding of Industrial Mineral Fillers" (UP-07-005;DSS File No. 14SQ.23440-7-9177) was initiated on November 3, 1987.

The economical background for this contract is the constantly growing demand for surface modified industrial mineral fillers for the plastics industry (1,2,3). Finely ground surface modified industrial minerals offer advantages over conventional fillers, because they disperse easier in plastic resins and reinforcing by surface compounding with the plastic matrix. As "functional" fillers they represent a value-added product, which can be sold at higher prices than normal grades.

The most common practice for surface modifying is to add suitable surface active reagents to the ground filler in a separate mixing stage. To date, mostly expensive reagents such as silanes, titanates, zircoaluminates and organo-silicones are used as surfactants as well as chlorinated paraffins, fatty and polymeric esters (3).

In the studied "mechanochemical" grinding process, the freshly fractured surfaces of the mineral filler contain active species that can react with organic solvents of low molecular weights or to form monomers or polymers that are "grafted" onto the mineral filler surfaces. This method potentially will reduce the cost of chemically modified mineral fillers by replacing the relatively more expensive coupling agents with lower amounts of cheaper organic solvents, as well as by avoiding the mixing stage with the surface modifiers.

At present, only silica is known to be studied for its capability for mechanochemical reactions with alkenes and alcohols (4,5). In some of these studies, it was found that the amount of water present in the mill may play a critical role in the success of the process.

2. TEST WORK UNDERTAKEN

Four minerals which originated from as many Canadian provinces as possible were selected and obtained for the project. They were:

- Silica from Selkirk Silica, Manitoba
- Talc from Steetley Talc, Ontario
- Calcite from Steep Rock Calcite, Ontario
- Mica (Phlogopite) from Suzorite Mica, Quebec

The test work was focused on three areas of investigation. These three areas were: establishing the optimum grinding conditions for each industrial mineral at a targeted particle size distribution, grinding each industrial mineral with various organic solvents at the optimum conditions and evaluating the ground products for "effective" alteration of the mineral surface properties.

2.1. Optimum Grinding Conditions

The optimum grinding condition for each industrial mineral will vary for two reasons. First, because of the relative hardness of each mineral and second because the particle size distribution desired for each mineral is different for their particular areas of application. The targeted size distribution for each industrial mineral was chosen in consultation with each mineral supplier. The targeted size distributions for each mineral are as follows:

*silica, approx. 95% - 45 um (=d_{95})
*talc, approx. 50% - 6 um (=d_{50})
95% - 17 um (d_{95})
*calcite, approx. 95% - 45 um (d_{95})
50% - 3.6 um (d_{50})
*phlogopite approx. 50% - 45 um (d_{50})
99% - 150 um (d_{99})

Laboratory size (24 cm diameter) ceramic mills have been selected for the test work. Grinding media which has been used for the test work consisted of Alumina bearing cylindrical bodies, having a diameter of 1.11 cm and a length of 1.27 cm. A standard media charge of 8 kg has been used for all grinding tests. This charge occupied approximately 45% of the ceramic mill volume.

The test work focused on varying the grinding time and mineral charge (on a weight basis). A total of 37 tests grinds have been conducted on the silica, talc, calcite, and phlogopite (mica) material. The parameters were chosen by regression analysis (see Appendix) according to the following grid:

mineral charge	grinding time (min):		
(Kg)	15	30	60
0.5	--*)	--	--
1.0	--	--	--
1.5	--	--	--

*) ground sample data

2.2 Organic Grinding

2.2.1. Selection of Additives

Candidate organic solvents have been selected and obtained for the test work. The organic solvents were selected on the basis of their potential compatibility with polypropylene; a polymer presently experiencing a high growth rate. The organic solvents were selected from the alcohols, ketones, ethers and carboxylic acid organic functional groups and all contain the "propyl" carbon chain. A paraffinic solvent kerosene was used as a blank.

The organic solvents selected and obtained for the project are as follows:

* isopropanol
* methyl isopropyl ketone
* di-isopropyl ether
* propionic acid
* Kerosene

The formulae and some properties of the chosen organic additives and of competing compounds that are present in the grinding stage are shown in Table 2.1. Excepting for kerosene, the molecular weights of the additives are significantly small. Their boiling points are between 68 and 220°C and allow normal handling. High ionization potentials of propionic acid (carboxylic) and propanol (alcohol) indicate that these additives are capable to form chemical bondings of higher stability. Possible surface reactions of the chosen organic additives with silica are shown in Fig. 2.1. and for calcite in Fig. 2.2.

2.2.2. Grinding Conditions

Exploratory organic grinding tests were conducted with 3g of organic additive per 1 kg mineral.

Further exploratory test work was conducted on silica, using a different mill having a of higher energy input was tested. This test consisted of grinding silica with and without additive in a vibratory disc mill. The evaluation of the product was the same as for mechanochemical grinding under standard conditions. The vibratory grinding conditions were: 100 ml steel disc mill, 5 minutes grinding time, 50 g sample, additive 0.5 g propanol.

For further parameter studies, standard grinding of silica with different water content, with and without additives, was conducted. Similar study was conducted on calcite, since calcite represents a crystal lattice having predominantly ionic bonding whereas covalent bonding prevails in silica.

Grinding studies for the determination of the optimum additive amount were carried out with the best performing mineral-additive combination.

For further proof of the mechanochemical grinding process and to investigate possible surface aging, surface treatment in aqueous solutions was tested at three different time intervals (0, 1 and 24 hours), after blank standard grinding of each mineral. The conditions for the treatment were 30 min. reaction time at 20°C in a stirred slurry; with 100 ml H_2O, 20g blank grinding product and 1g of the best performing organic additive.

A total of 24 scoping tests at optimized standard conditions (see Section 3.1.) was carried out with all minerals including blank sample tests and 2 additional tests with silica using a different mill type. The grinds of calcite and silica at varying parameters amounted to 18 tests.

2.3. Product Characterization

The ground products and head samples were submitted for particle size analysis. For coarse materials the particle size distribution was determined mainly by screen analysis, whereas the finer grained products (-100 mesh) were measured by sedigraph analysis. The comparison of sedigraph analyses with wet screening on a 500 mesh screen revealed that the equivalent diameters obtained from the sedigraph were generally smaller than the diameters from screen analysis. The deviation factor for silica and calcite was approx. 1.2 and for talc and phlogopite 2.4. However, because of its common use in the mineral filler industry the equivalent particle size from sedigraph analysis remained as the preferred parameter for particle size characterization. A key factor that influences the surface properties of a mineral is the specific surface area. This was determined for all samples from the organic grinding program by BET or by correlating BET-measurements and particle size distributions by regression analysis. Additionally, the head samples were measured for their BET-surface area (where applicable) and moisture content.

The oil of adsorption Packing Fraction (8)and, occasionally, the Daniel flow point measurements formed the basis to evaluate the "effectiveness" for the various organic additives employed (6 to 10/see also Appendix).

They were performed prior to and after an attempt to extract the solvent from the mineral surface, using boiling distilled water and alcohol at room temperature. Extraction conditions were 100 ml per 10 g sample and a time of 2 hours. Linseed oil and mineral oil were used in the "oil adsorption titration" and modified "Daniel flow point titration". Raw linseed oil is considered as a polar type oil, density 0.93 g/ml; while motor oil ("Formula 2000"/Imperial oil Ltd. SAE 5W30) is considered as a non-polar type oil, density 0.85 g/ml.

The "indirect methods" (oil adsorption, Packing Fraction and flow point) are strongly related to the specific surface area of the sample. Since additives might have a significant influence on the grinding performance, the classical determination of oil adsorption and flow point can yield misleading interpretations, if applied exclusively. A solution is perhaps given by comparing the oil adsorption values for dominantly non-polar (motor oil) and a dominantely polar oil (linseed oil) (see Ferrigno 1982,8). The resulting evaluation criterion is a relative adsorption number derived by dividing the non-polar oil adsorption value by the polar oil of adsorption value. For example, a relative adsorption number lower than that of the sample which was ground without additive, indicates an increased wetability by non-polar resins (ie it takes less oil to completely coat or wet each mineral particle).

Another approach to solve the above mentioned problem is to relate the oil of adsorption and flow point numbers to the sample surface (g oil/m^2) instead of the sample weight (lbs oil/100 lbs). In every case, a significantly low oil uptake to wetten or disperse a surface treated ground material (when compared to a blank with the same surface area) indicates improved surface properties for its utilization as plastic filler (11).

All possible evaluation methods were tested for silica and it was found that the surface related mean "oil of adsorption" values are the most reliable data (see Section 3.1. Silica).

Filler performance tests using the most promising products from organic grinding compared to the blank samples determined the effectiveness of the surface treatment. The filler performance tests consisted of comparing the evaluated parameters of the products to commercial products. Evidence of surface coating and chemical bonding of the organic additive to the mineral surface was also evaluated using infrared spectroscopy and Thermo Gravimetric Analysis methods.

TABLE 2.1.

SELECTION OF ORGANICS

additive	formula	mol wt.	boiling point °C	ionization potential eV
propanol	$CH_3CH_2CH_2OH$	60.11	97.4	10.15
propionic acid	$CH_3CH_2CH_2OOH$	74.08	141	10.24
di-iso-propyl-ether	$[CH_3]_2CHOCH[CH_3]_2$	102.18	68	9.20
methyl-iso-propyl ketone	$i\text{-}C_3H_7COCH_3$	86.14	94.5	9.30
kerosene	$C_{13}H_{28}$	184	220	8
	others:			
oxygen	O_2	32	--	12.06
water	H_2O	18	100	12.6

FIG. 2.1.
SURFACE CHEMISTRY

POSSIBLE CHEMICAL SURFACE REACTIONS
(simplified, applied to 1st. molecular layer)

silica	SiO_2 :	
$-O_2$	--	
water:	$Si_4O_8 + 2H_2O$	$Si_4O_6\ (OH)_4$
H_2O		
propanol:	$Si_4O_8 + 4ROH$	$Si_4O_6(RO)_4 + 2H_2O$
ROH	$Si_4O_6\ (OH)_4 + 4ROH$	$Si_4O_6(RO)_4 + 4H_2O$
propionic acid:	$Si_4O_8 + 4ROOH$	$Si_4O_6(ROO)_4 + 2H_2O$
ROOH	$Si_4O_6\ (OH)_4 + 4ROOH$	$Si_4O_6(ROO)_4 + 4H_2O$
ether :	$Si_4O_8 + 4RO\text{-}OR$	$Si_4O_6(ROO)_4 + 2H_2O$
ROR	$Si_4O_6\ (OH)_4 + 2ROR$	$Si_4O_6(RO)_2\ RO\ _2 + 2H_2O$
ketone :	$Si_4O_8 + 2\ RCOR$	$Si_4O_6(RCO)_2\ R_2$
RCOR	$Si_4O_6\ (OH)_4 + 2RCOR$	$Si_4O_6(RCO)_2\ R_2 + 2H_2O$
	$Si_4O_8 + 2RCOR$	$Si_4O_6(O_2CRR)_2$
	$Si_4O_6\ (OH)_4 + 2RCOR$	$Si_4O_6(O_2CRR)_2 + 2H_2O$
kerosene :	$Si_4O_8\ 2R_2$	$Si_4O_6(RO)_2\ R_2$
R_2	$Si_4O_6\ (OH)_4 + 2R_2$	$Si_4O_6(RO)_2\ R\ _2 + 2H_2O$

R = carbon hydrogen group C_nH_{2n+1}

FIG. 2.2.
SURFACE CHEMISTRY

POSSIBLE CHEMICAL SURFACE REACTIONS
(simplified, applied to 1st. molecular layer)

calcite	$CaCO_3$:	
$-O_2$	--	
water: H_2O	$CaCO_3+2H_2O$	$(Ca(OH)_2 + H_2CO_3$
propanol: ROH	$CaCO_3$ + ROH (Ca,H) (CO_3, OH) + ROH	(Ca,R) (CO_3,OH) (Ca,R) (CO_3,OH) + H_2O
propionic acid: ROOH	$CaCO_3$+ ROOH (Ca,H) (CO_3,OH)+ ROOH	(Ca,H) (CO_3, ROO) (Ca,H) (CO_3,ROO) + H_2O
ether : ROR	$CaCO_3$ + ROR (Ca,H) (CO_3,OH) + ROR	(Ca,R) (CO_3,RCO) (Ca,R) (CO_3,RO) + H_2O
ketone : RCOR	$CaCO_3$ + RCOR (Ca,H) (CO_3,OH) + RCOR	(Ca,R) (CO_3,RCO) (Ca,R) (CO_3,RCO) + H_2O
kerosene : R_2	$CaCO_3$ + R_2 (Ca,H) (CO_3,OH) + R_2	(Ca,R^+) (CO_3,R^-) (Ca,R^+) (CO_3,R^-) + H_2O

R = carbon hydrogen group C_nH_{2n+1}

3. RESULTS AND DISCUSSION

3.1. Optimum Grinding Conditions and Organic Grinding

Depending on the size distribution and hardness of the feed as well as the targeted size distribution, the optimum grinding time and mineral charge was different for every mineral. Due to too coarse head samples, oversize particles had to be removed by screening at 100 mesh from the grinding products of calcite and mica (phlogopite).

Besides a numeric comparison of data, the test results for organic grinding were analysed by graphic correlations of their differences between a standard blank grinding product and the rank of ionization potential of the mineral surface and the organic additives. The differences were obtained by subtraction of the evaluation parameter values for the blank grinding product from those of the corresponding organic grinding products. Other graphical correlations comprise the influence of water content of the mineral charge and of the amount of organic additive.

3.1.1. Silica

The head sample shows a low moisture content of 0.09% and a narrow particle size distribution resulting in a relatively low BET- surface area measure of 0.127 m^2/g . The particle size analyses of the ground products are presented in Appendix B. The d_{95} particle sizes (95% passing the according screen size) are presented in Table 3.1. At a 60 minute grinding time and 0.5 kg mill charge, a sufficient d_{95} of 43 microns (um) (below the 45 um - criteria) was reached . However, at these grinding conditions ceramic splinters from the mill were observed. To overcome this problem, 0.75 kg mill charge and 90 minute grinding time was chosen, on the basis of regression analysis (explained in appendix A) as standard grinding conditions for silica. The corresponding screen analysis of the standard grind product is shown in Appendix B. Minor mill abrasion was still observed. The Al_2O_3 contents for the head and standard ground product were 2.28% and 2.59% respectively (repeat Assay: 2.23% & 2.64% Al_2O_3).

The test results for the organic grinding of silica with the various additives are shown in Table 3.2. and in a condensed form (as mean values were applicable) in Table 3.3. The studied evaluation parameters are the oil of adsorption (lbs oil/100 lbs, g oil/m^2), Packing Fraction (PF), the Daniel flow point (lbs oil/100 lbs, g oil/m^2) and the relative adsorption number (lbs motor oil/lbs linseed oil). Their differences to the blank grinding product are correlated with the rank of ionization potential in Figs. 3.1 to 3.5.

As can be seen in Figs 3.1 and 3.3 as well as Table 3.3, the oil of adsorption, flow point and Packing Fraction values do not show any significant trend, when related to the sample mass (lbs oil/100 lbs). This is due to the varying surface area for each individual grind, as indicated by the results given in Tables 3.2. and 3.3. By relating the evaluation parameters to the surface area (g oil/m^2) this problem is solved. This is shown in Figs 3.3. and 3.4. Both show a tendency towards a minimum oil uptake for grinding with propanol. Since this trend is more pronounced for the oil of adsorption it is evident that the oil absorption works more accurately than the Daniel flow point determination.

In Fig. 3.5. the relative adsorption number and the mean oil of adsorption values for the organic grinding of silica are compared. The relatively small differences in polarity of the two oil types used, lead to unreliable and even contradicting results for the oil of adsorption number. In contrast, the mean surface related oil of adsorption values show a distinct minimum oil uptake for the grinding with propanol, indicating that it is the most 'effective' additive for silica. In most cases (except for kerosene and ether) desorption tests lead to a further drop or oil of adsorption values (see Fig. 3.5.). This indicates the existence of a physically adsorbed surplus of organic additive, which acts as oil solvent, unless it has been removed through desorption. The relatively high ionisation potential of the weak base propanol provides the conditions for its stable chemical bonding to the surface of silica; enhanced by the tendency of silica to react like a weak acid. This weakly acidic behaviour of silica also explains the better performance of propanol as a surfactant when compared to propionic acid.

Based on the findings for silica the mean surface related oil of adsorption values formed the basis of test evaluation. The Daniel flowpoint, Packing Fraction and relative adsorption number are reported to back up the results.

The effect of applying a higher specific energy input to the mechanochemical grinding process was investigated with a vibratory disc mill (Table 3.4.). The reason for the higher oil of adsorption values for vibratory grinding with propanol might be higher mill abrasion as a darker color of the according grinding product was observed. Fine steel powder from wear of the vibratory disc mill can add significantly to the oil of adsorption value of the grinding products; due to the high affinity of oils to fresh metal surfaces.

To study the influence of water in the grinding process, standard grinding tests were conducted with different water contents of the mineral charge. This study comprised a test series of blank sample grinding with 3g propionic acid and propanol per kg mineral charge. The results are shown in Table 3.5. and Fig. 3.6.

It is obvious, that propanol and propionic acid caused significantly lower oil of adsorption values than those of the blank sample only in the dry grinding tests. Wet grinding caused in general, a reverse effect. It should be noted that the minimum oil of adsorption value for the wet blank grinding occurs at a water content of 10% of the mineral charge. This marks an area of disadvantageous grinding conditions, which causes also a minimum surface area of the grinding product due to poor solids dispersion in the mill (caking of charge and grinding media).

The results of wet surface treatment of silica after blank standard grinding and after different aging times of the grinding product are given in Table 3.6. The average differences of the oil of adsorption values to the untreated blank sample did not show any major trends. They seem to reflect on the standard deviation of the oil of adsorption measurement. Furthermore the wet surface treatment seemed to result in an increased oil of adsorption values rather than in improved surface modification of silica. This supports the previous finding that the mechanochemical grinding of silica with the various organic additives works only as a dry process and indicates that it is superior to the addition of the additives after the grinding stage.

3.1.2. Talc

The moisture content and BET-surface area of the talc head sample was found to be 0.16% and 1.782 m^2/g respectively. These results are higher than that of the silica due to the finer particle size distribution (see Appendix C). Because of the fine initial particle size distribution, all size distribution measurements in the ground talc were measured by sedigraph analysis (see Appendix C). The d_{50} particle sizes (50% smaller this size) are shown in Table 3.7. None of these tests reached the required size of 6 um. Consequently the chosen standard grinding conditions were a 0.5 kg mill charge and 75 min grinding time. They were estimated by regression analysis.

The results for the organic grinding of talc are given in Tables 3.8. and 3.9. and in Fig. 3.7. All applied additives appeared to improve (lower) the oil uptake of the ground products, in almost equal amounts. This as well as no significant changes after desorption indicates, that chemisorption of the organic additives at the talc surface is not predominant. Specific surface reactions could be otherwise noted.

Propionic acid seems to result into more favorable improvements, because of the low oil of adsorption values of the according grinding product, which are not increased after desorption (Table 3.9.).

The wet surface treatment of the talc with propionic acid after a standard blank grind is apparently influenced by the aging of the talc surface (Table 3.10.). For immediate surface treatment after grinding, lowered oil adsorption values are reported. After 1 hour as well as 24 hours aging at room temperature and exposure to air equally increased oil of adsorption values occur after surface treatment. Although showing a trend, these effects are relatively small.

3.1.3. Calcite

A moisture content of 0.0% and a very coarse particle size distribution with 50% - 2.28 mm are characteristic for the calcite head sample. The screen analyses for the grid tests show that the projected particle size distribution of 95% passing 325 mesh was not reached (Table 3.11, Appendix D). Consequently the prolongation of the grinding time to 70 minutes and a mineral charge of 0.5 kg was chosen as the optimum calcite grinding condition, on the basis of regression analysis. During the grinding intense coating of the mill and grinding media with finely ground calcite was observed. This leads to residual fractions of oversize particles of up to 3 mm in diameter. To overcome this problem, screening to -100 mesh was necessary.

The characterization of the products from organic calcite grinding, is shown in Tables 3.12. and 3.13. and in Figure 3.8. The results clearly point out that propionic acid was the most effective additive causing the lowest resulting oil of adsorption values. A surplus of non chemically bonded propionic acid can be concluded from the improvement after desorption. Repelling forces at the calcite surface could be responsible for adverse effects by adding propanol to the grinding stage. Too low reactivities rates might explain the poor improvement by isopropylether and methyl isopropyl ketone, whereas the behaviour of kerosene could be due to physisorption.

Wet standard grinding of calcite with propionic acid leads to increased oil of adsorption values (Table 3.14., Fig. 3.9.). This might be caused by the formation of highly water soluble hydrated calcium propionate. Complete dehydration by heating (120°C) renders a small increase of oil uptake of calcite ground with propionic acid as well as without any additive. An increase in mineral surface charges, typically by superdry grinding, could explain this phenomenon. Higher electrostatic surface charges can cause induced polarization and orientation in electrical non conducting liquids such as oil, leading to a higher viscosity and therefore higher oil uptake.

The results for the standard grinding of calcite with varying additions of propionic acid are shown in the Tables 3.15. and 3.16. and Figure 3.10. An optimum range of minimized oil of adsorption values occurs between 0.6g and 10g propionic acid per kg feed material. The difference between the oil of adsorption before desorption to that after desorption (oil of adsorption see Fig. 3.10.) is positive for additions of propionic acid above 0.9 g/kg. At a given surface area of 2.6 m^2/g of the calcite and an estimated space requirement of 25 A^2 of each molecule of propionic acid bonded to the calcite surface the amount of 0.9 kg propionic acid per kg calcite equals to a coverage of 70% of the calcite surface by a monomolecular layer of chemically bonded propionic acid. This supports the idea, that improved (lower) oil of adsorption values after desorption tests are mainly caused by the previous removal of not chemically bonded surplus additives in the desorption stage. The lowest oil of adsorption was measured for calcite grinding with 3 g/kg addition of propionic acid.

Aging of the ground blank at room temperature and air exposure showed a pronounced effect on wet surface treatment with propionic acid (Table 3.16.). Similar in behaviour of talc, surface treatment immediately after grinding yielded improved oil adsorption values. The oil uptake increased to comparable values after 1 and 24 hours aging time. Hydration of the calcium ions at the mineral surface might be the reason for this behaviour, due to the high water solubility of resulting hydrated calcium propionate.

3.1.4. Mica (Phlogopite)

The head sample of the phlogopite material contained no moisture and represented a narrow particle size class between 20 and 65 mesh. Consequently it was necessary to classify the products to -100 mesh in order to meet the targeted particle size distribution. The results for establishing the grinding conditions (Table 3.18.) led to the standard conditions of 25 min grinding time and 0.5 kg mineral charge.

Since the chosen mica (phlogopite) contains calcium cations, propionic acid proved to be the best performing organic additive in lowering the oil of adsorption value (Tables 3.19.,3.20., & Fig. 3.11.) during dry grinding. Organic grinding with isopropylether seemed to result in an organophobic surface behaviour of the phlogopite. The reason for this might be the amphoteric character of isopropyl ether. All other additives had no significant influence on the oil of adsorption.

Wet surface treatment after blank grinding of phlogopite was tried with propionic acid (Table 3.21.) after varying the aging time. In all cases, higher oil of adsorption values than that of the blank sample were determined. There is an obvious trend of increasing oil uptake with longer ageing times. This might be explained by reaction of propionic acid with hydrated potassium ions from the phlogopite surface in the presence of water.

3.1.5. Selection of Best Filler Additive Combination

Table 3.21. summarizes the best performing mineral additive combinations and the resulting improvement for each industrial mineral filler. The overall improvement increased from silica, phlogopite (mica), talc and calcite as the highest.

Except for silica, propionic acid is the most effective additive. Its effectiveness is apparently dependant on the prevailing bond type in the mineral lattices. These are

- ionic in calcite
- Van der Waals type, covalent and ionic in talc
- covalent and ionic in phlogopite
- covalent in silica

Ionic bonding and the amount of available calcium or magnesium ions seem to be the basic condition for chemical adsorption of propionic acid by the formation of calcium or magnesium propionate at the surfaces of calcite and phlogopite. Improved oil of adsoprtion after desorption as an indicator for chemical bonding supports this idea (see Table 3.22.). Talc does not show improvement after desorption, which points out physical Van der Waals bonding as the main active mechanism in the organic surface modification of this mineral. The Van der Waals forces in the talc lattice occur within layers between chemically saturated Si-Al-oxide layers which enclose the Magnesium and hydroxyl ions of this mineral. Cleavage occurs along the Van der Waals bondings. Therefore chemisorption of additives is likely to take place rather at the edges of the talc platelets than along the cleavage.

Propanol, which is the best additive for silica, seems to bond chemically to the surface of silica. This can be inferred from improved oil of adsorption after desorption tests and might be due to the slightly acidic behaviour of the surface. The reason for the low overall improvement of the surface modification of silica by propanol could be the fact that propanol has to compete with the natural hydration of the surface of silica.

With the highest overall improvements as well as improvements after desorption tests the combination of calcite as filler and propionic acid as organic additive appears to be most promising.

3.2. POLYMER/FILLER PERFORMANCE

3.2.1. Performance Tests

The tests to evaluate the performance potential of the most promising products from the conducted test work as plastic fillers are based on comparisons with comprehensive surface modified commercial plastic fillers and the according initial untreated products from the standard blank grinding tests. They consisted of adsorption methods (ASTM D 281 & D 1755) to judge blending properties and of infrared spectroscopy (DRIFT) to prove the nature of the bonding of the surface modifiers to the surfaces of the various mineral fillers as well as Thermogravimetric Analysis (TGA).

Table 3.23. shows the surface properties of ground talc products obtained from the testwork in comparison with a surface modified commercial talc grade (Micro Pflex 1200/Pfizer). In spite of their higher surface area, the commercial talc grades render higher surface related oil absorptions than the coated product from mechanochemical grinding and therefore lower improvements against the blank sample.

In Table 3.24. the calcite products from the grinding test work are compared to comprehensive commercial calcite grades (Pluess-Stauffer, Pfizer). Except for the uncoated material all shown surface areas are similar. The oil of adsorption values of the coated products are remarkably lower than those of the respective uncoated materials thus proving the validity of the surface related oil of adsorption as an evaluation parameter for prospective plastic fillers. The improvements of surface modification against the comprehensive untreated materials are in the range of 40 to 55%. An interesting finding is the oil adsorption increasing effect of desorption tests on the commercial surface modified calcite products. This might be due to the common practise to use watersoluble stearate or palmitate salts as modifying reagents.

The infrared absorption spectra did not show any distinct differences between surface modified and unmodified materials, including the commercially available reference samples. The same difficulties were encountered, when Thermogravimetric Analysis (TGA) was tried on selected calcite filler samples. This leads to the conclusion that the amount of the surface modifying compounds within the samples is too small to be detected by the chosen methods. Alternative methods of higher sensitivity such as Mass Spectometry are not able to give direct evidence, because of the necessary removal of the surface compounds prior to their analysis (details in Appendix F).

TABLE 3.1.
ESTABLISH GRIND CONDITIONS
SILICA

mill charge	d_{95} for: 15 min grind	30 min grind	60 min grind
0.5 kg	100 um	76 um	43 um*)
1.0 kg	220 um	145 um	82 um
1.5 kg	265 um	170 um	135 um

NOTES

1) Targeted particle size distribution of 95% passing 45 um (d_{95})

2) *mill abrasion

3) size distribution of head sample:
50% -144 um (=d_{50}), 95% - 291 um (=d_{95})
moisture content: 0.09%

4) selected grinding conditions based on regression analysis:
90 min grinding time
0.75 kg mineral charge

5) Details in Appendix B

TABLE 3.2.
ORGANIC GRINDING AND CHARACTERIZATION OF SILICA

additive	desorption media	calculated surface area	oil of adsorption (g/m^2)		Packing Fraction (PF)		flow point (g/m^2)	
			linseed oil	motor oil	linseed oil	motor oil	linseed oil	motor oil
-------*)	----	0.754	0.221	0.203	0.682	0.681		
-------	H_2O	"	0.214	0.225	0.689	0.658		0.367
-------	alcohol	"	0.225	0.225	0.678	0.658		0.367
propanol	----	0.901	0.185	0.170	0.682	0.681		
"	H_2O	"	0.166	0.166	0.705	0.686		0.284
"	alcohol	"	0.166	0.189	0.705	0.658		0.333
propionic acid	----	0.785	0.213	0.195	0.681	0.681		
" "	H_2O	"	0.205	0.217	0.690	0.657		0.353
" "	alcohol	"	0.191	0.217	0.705	0.657		0.382
ether	----	0.872	0.181	0.175	0.694	0.682		
"	H_2O	"	0.172	0.195	0.705	0.658		0.344
"	alcohol	"	0.172	0.172	0.705	0.686		0.344
ketone	----	0.849	0.186	0.180	0.694	0.681		
"	H_2O	"	0.192	0.177	0.687	0.685		0.302
"	alcohol	"	0.192	0.177	0.687	0.685		0.326
kerosene	----	0.665	0.224	0.218	0.706	0.693		
"	H_2O	"	0.245	0.226	0.687	0.685		0.385
"	alcohol	"	0.245	0.226	0.687	0.685		0.385

*) blank

NOTES:

1) Detailed particle size analyses in Appendix B

TABLE 3.3.

ORGANIC GRINDING OF SILICA

(mean values and selected data)

organic additive	average oil of adsorption (g/m^2)		average Packing Fraction (PF)		initial relative adsorption number (motor oil/ linseed oil	d_{50} (um) ****)	surface area (m^2/g)
	before desorption*)	after desorption**)	before desorption*)	after desorption**)			
--- ***)	0.212	0.222	0.682	0.671	0.916	14.2	0.754
propanol	0.178	0.172	0.682	0.689	0.916	11.3	0.901
propionic acid	0.204	0.208	0.681	0.677	0.916	13.5	0.785
ether	0.178	0.178	0.688	0.689	0.968	11.8	0.872
ketone	0.183	0.185	0.688	0.686	0.968	12.2	0.849
kerosene	0.221	0.236	0.700	0.686	0.973	16.7	0.665

*) mean of 2 values

**) mean of 4 values

***) blank

****) detailed particle size analyses see Appendix B

TABLE 3.4.
ORGANIC GRINDING OF SILICA IN A VIBRATORY DISC MILL.

additive	d_{50} (mm) **)	surface area (m^2/g)	oil of adsorption (g oil/m^2)		Packing Fraction	
			linseed oil	motor oil	linseed oil	moto oil
-----*)	0.0073	1.267	0.110	0.101	0.720	0.7
propanol	0.0082	1.157	0.121	0.111	0.719	0.7

*) blank

**) see sedigraph analyses in Appendix

Note:

detailed particle size analysis in Appendix B

TABLE 3.5.
ORGANIC AND BLANK GRINDING OF SILICA
AT VARYING WATER CONTENTS
Characterization of products

amount of water in grinding	additive	calculated surface area (g/m^2)	oil of adsorption (g/m^2)		flowpoint (g/m^2)		Packing Fraction (PF)	
			linseed oil	motor oil	linseed oil	motor oil	linseed oil	motor oil
0%H_2O	-------	0.785	0.213	0.173	0.344	0.358	0.570	0.538
0.09%H_2O	-------	0.754	0.221	0.203	0.382	0.385	0.554	0.530
10% "	-------	0.680	0.178	0.150	0.328	0.363	0.616	0.570
25% "	-------	0.889	0.188	0.182	0.324	0.326	0.554	0.530
37.5% "	-------	0.969	0.192	0.185	0.308	0.317	0.546	0.516
0%H_2O	propionic acid	0.750	0.187	0.181	0.372	0.364	0.570	0.545
0.09% H_2O	"	0.785	0.213	0.195	0.367	0.369	0.554	0.530
10% "	"	0.518	0.216	0.181	0.431	0.444	0.616	0.587
25% "	"	0.889	0.200	0.198	0.369	0.367	0.522	0.501
37.5% "	"	0.895	0.229	0.219	0.415	0.401	0.491	0.477
0%H_2O	propanol	0.920	0.161	0.158	0.303	0.315	0.562	0.530
0.09%H_2O	"	0.901	0.185	0.170	0.310	0.303	0.562	0.545
10% "	"	0.601	0.186	0.170	0.371	0.383	0.616	0.587
25% "	"	0.818	0.227	0.208	0.375	0.364	0.538	0.523
37.5% "	"	1.032	0.199	0.190	0.289	0.289	0.545	0.523

Note:

detailed particle size analysis in Appendix B

TABLE 3.6.

EFFECT OF SURFACE TREATMENT OF SILICA AFTER STANDARD GRINDING AT DIFFERENT AGING TIMES (SURFACE TREATMENT WET IN STIRRED BEAKER FOR 30 MIN IN 100 ml H_2O, WITH 1g ADDITIVES AND 20g SAMPLE.

aging time (hrs)	additive	oil of adsorption			average difference to blank sample (%)	Packing Fraction (PF)	
		linseed oil	motor oil	average		linseed oil	motor oil
0	-------*)	0.206	0.214	0.210	0.0	0.697	0.670
"	propionic acid	0.219	0.214	0.217	+3.3	0.684	0.670
"	propanol	0.233	0.225	0.229	+9.0	0.671	0.658
"	ether	0.206	0.213	0.210	0.0	0.697	0.671
"	ketone	0.206	0.225	0.216	+2.9	0.697	0.658
1	propionic acid	0.219	0.200	0.210	0.0	0.684	0.684
"	propanol	0.206	0.200	0.203	-3.3	0.697	0.684
"	ether	0.233	0.200	0.217	+3.3	0.671	0.684
"	ketone	0.232	0.225	0.229	+9.0	0.672	0.658
24	propionic acid	0.219	0.214	0.217	+3.3	0.684	0.670
"	propanol	0.206	0.225	0.216	+2.9	0.697	0.658
"	ether	0.206	0.225	0.216	+2.9	0.697	0.658
"	ketone	0.219	0.213	0.216	+2.9	0.684	0.671

*) blank

TABLE 3.7.
ESTABLISH GRIND CONDITIONS OF TALC

mill charge	d_{50} for: 15 min grind	30 min grind	60 min grind
0.5 kg	18 um	12.5 um	8.3 um
1.0 kg	18 um	12.6 um	11.5 um
1.5 kg	18 um	15.5 um	13.8 um

NOTES

1) Talc particle size distribution of 50% passing 6 um (d_{50})

2) size distribution of head sample:
50% - 19 um (=d_{50}), 95% -56 um (=d_{95})
moisture content: 0.16%

3) selected grinding conditions (based on regression analysis):
75 min grinding time
0.5 kg mineral charge

4) detailed particle size analyses in Appendix C

TABLE 3.8.
ORGANIC GRINDING AND CHARACTERIZATION OF TALC

additive	desorption media	calculated surface area	oil of adsorption (g/m^2)		Packing Fraction (PF)		flow point (g/m^2)	
			linseed oil	motor oil	linseed oil	motor oil	linseed oil	motor oil
-------*)	----	4.82	0.059	0.058	0.543	0.521		0.149
-------	H_2O	"	0.057	0.062	0.552	0.508		0.146
-------	alcohol	"	0.062	0.062	0.531	0.508		0.141
propanol	----	7.68	0.040	0.039	0.524	0.508		0.101
"	H_2O	"	0.042	0.039	0.512	0.508		0.094
"	alcohol	"	0.039	0.039	0.530	0.508		0.094
propionic acid	----	7.74	0.039	0.039	0.528	0.506		0.091
" "	H_2O	"	0.036	0.039	0.548	0.506		0.093
" "	alcohol	"	0.041	0.041	0.516	0.493		0.088
ether	----	7.81	0.035	0.038	0.553	0.510		0.091
"	H_2O	"	0.038	0.038	0.533	0.510		0.087
"	alcohol	"	0.041	0.041	0.514	0.491		0.090
ketone	----	7.81	0.036	0.038	0.546	0.510		0.092
"	H_2O	"	0.041	0.041	0.514	0.491		0.090
"	alcohol	"	0.038	0.041	0.533	0.491		0.087
kerosene	----	7.26	0.041	0.041	0.532	0.509		0.099
"	H_2O	"	0.041	0.041	0.532	0.509		0.094
"	alcohol	"	0.044	0.041	0.514	0.509		0.097

*) blank

Note:

detailed particle size analysis in Appendix C

TABLE 3.9.
ORGANIC GRINDING OF TALC
(mean values and selected data)

organic additive	average oil of adsorption (g/m^2) before desorption*)	after desorption**)	initial relative adsorption number (motor oil/linseed oil)	d_{50} (um) ****)	surface area (m^2/g)
--- ***)	0.059	0.061	0.986	13.5	4.82
propanol	0.040	0.040	0.983	8.8	7.68
propionic acid	0.039	0.039	1.00	8.7	7.74
ether	0.037	0.040	1.080	8.6	7.81
ketone	0.037	0.040	1.046	8.6	7.81
kerosene	0.041	0.042	1.00	9.5	7.26

*) mean of 2 values

**) mean of 4 values

***) blank

****) see sedigraph analysis in Appendix C

TABLE 3.10.
EFFECT OF SURFACE TREATMENT OF TALC AFTER STANDARD GRINDING AT DIFFERENT AGING TIMES (SURFACE TREATMENT WET IN STIRRED BEAKER FOR 30 MIN IN 100 ml H_2O, WITH 1g ADDITIVES AND 20g SAMPLE.

ging time (hrs)	additive	oil of adsorption			average difference	Packing Fraction (PF)	
		linseed oil	motor oil	average	to blank sample (%)	linseed oil	motor oil
0.0	--------	0.071	0.067	0.069	0.0	0.497	0.489
0.0	propionic acid	0.066	0.064	0.065	-5.8	0.515	0.500
1.0	"	0.070	0.074	0.072	+4.3	0.501	0.464
24.0	"	0.073	0.071	0.072	+4.3	0.490	0.475

TABLE 3.11.
ESTABLISH GRIND CONDITIONS OF CALCITE

mill charge	wt % - 325 mesh for:		
	15 min grind	30 min grind	60 min grind
0.5	--	27.9%	49.25%
1.0	21.4%	38.2%	69.1%
1.5	31.0%	56.1%	90.2%

NOTES

1) Targeted particle size distribution of 95% -325 mesh (= -45 um)

2) size distribution of head sample:
50% -2.26 mm (d_{50}), 95% -7 mesh
(= - 2.8 mm)
moisture content: 0.0%

3) selected grinding conditions (based on regression analysis):
70 min grinding time
0.5 kg mineral charge
classifying to -100 mesh

4) detailed particle size analysis in Appendix D

TABLE 3.12.

ORGANIC GRINDING AND CHARACTERIZATION OF CALCITE

additive	desorption media	calculated surface area	oil of adsorption (g/m^2)		(lb/ oil/100 lb)		flow point (g/m^2)		Packing Fraction (PF)	
			linseed oil	motor oil	linseed oil	motor oil	linseed oil	motor oil	linseed oil	motor oil
-----*)	----	1.21	0.100	0.112	27.9	22.2	0.231	0.183	0.740	0.699
-----	H_2O	"	0.096	0.106	23.3	22.4	0.193	0.185	0.748	0.711
-----	alcohol	"	0.096	0.140	23.3	25.6	0.193	0.212	0.748	0.650
propanol	----	1.48	0.113	0.132	26.0	28.1	0.176	0.190	0.673	0.617
"	H_2O	"	0.110	0.130	25.6	29.8	0.173	0.201	0.679	0.621
"	alcohol	"	0.126	0.130	27.9	29.8	0.189	0.201	0.649	0.621
propionic acid	----	3.46	0.054	0.062	28.8	30.7	0.083	0.089	0.648	0.595
"	H_2O	"	0.047	0.055	27.9	29.8	0.081	0.086	0.679	0.623
"	alcohol	"	0.054	0.055	30.2	29.8	0.087	0.086	0.648	0.623
ether	----	1.36	0.089	0.100	23.3	21.3	0.171	0.157	0.740	0.698
"	H_2O	"	0.103	0.110	25.6	25.6	0.188	0.188	0.711	0.678
"	alcohol	"	0.085	0.094	23.3	22.4	0.171	0.165	0.749	0.711
ketone	----	1.35	0.096	0.107	22.3	22.2	0.165	0.164	0.727	0.685
"	H_2O	"	0.069	0.111	21.0	27.7	0.156	0.205	0.787	0.678
"	alcohol	"	0.104	0.111	23.3	25.6	0.173	0.190	0.710	0.678
kerosene	----	1.50	0.087	0.091	21.2	21.3	0.141	0.142	0.725	0.698
"	H_2O	"	0.093	0.100	23.3	23.4	0.155	0.156	0.712	0.677
"	alcohol	"	0.093	0.100	25.6	23.4	0.171	0.156	0.712	0.677

*) blank

Note:

detailed particle size analyses see Appendix D

TABLE 3.13.
ORGANIC GRINDING OF CALCITE
(mean values and selected data)

organic additive	average oil of adsorption (g/m^2) before desorption*)	after desorption**)	initial relative adsorption number (motor oil/linseed oil)	d_{50} (um) ****)	surface area (m^2/g)
---***)	0.106	0.110	1.1	8.5	1.21
propanol	0.123	0.124	1.15	6.3	1.48
propionic acid	0.058	0.053	1.17	5.8	3.46
ether	0.095	0.098	1.1	6.2	1.36
ketone	0.102	0.099	1.12	7.5	1.35
kerosene	0.089	0.097	1.05	8.4	1.50

*) mean of 2 values
**) mean of 4 values
***) blank
****) see sedigraph analysis in Appendix D

TABLE 3.14.

ORGANIC GRINDING OF CALCITE WITH PROPIONIC ACID AT VARYING WATER CONTENTS.

water content (%)	addition of propionic acid (g/kg)	d_{50} (mm)	calculated surface area (m^2/g)	oil of adsorption linseed oil	motor oil	($g\ oil/m^2$) mean	Packing Fraction (PF) linseed oil	motor oil
0.0 (heated)	0.0	0.009	1.21	0.116	0.134	0.125	0.710	0.660
0.0	0.0	0.0085	1.21	0.100	0.112	0.106	0.740	0.699
25.0	0.0	0.0064	2.85	0.085	0.081	0.083	0.587	0.577
0.0 (heated)	3.0	0.0068	2.63	0.067	0.068	0.068	0.662	0.638
0.0	3.0	0.0058	3.46	0.054	0.062	0.058	0.648	0.595
10.0	3.0	0.0103	1.23	0.151	0.159	0.155	0.650	0.617
37.5	3.0	0.009	1.57	0.142	0.152	0.147	0.607	0.569

Note:

detailed particle size analyses see Appendix D

TABLE 3.15.

ORGANIC GRINDING OF CALCITE WITH VARYING ADDITIONS OF PROPIONIC ACID.

addition of propionic acid (g/kg)	desorption with	d_{50} (mm)	calculated surface area (m^2/g)	oil of adsorption (g/m^2)		Packing Fraction (PF)	
				linseed oil	motor oil	linseed oil	motor oil
—	------	0.0085	1.21	0.100	0.112	0.740	0.699
0.2	------	0.009	1.21	0.138	0.134	0.674	0.660
0.6	------	0.0067	2.40	0.066	0.078	0.685	0.627
1.5	------	0.006	2.83	0.072	0.084	0.628	0.570
3.0	------	0.0058	3.46	0.054	0.062	0.648	0.595
10.0	------	0.0057	2.83	0.066	0.081	0.648	0.579
40.0	------	0.0094	1.39	0.127	0.144	0.661	0.611
--	H_2O	0.0085	1.21	0.096	0.106	0.748	0.711
0.2	"	0.009	1.21	0.135	0.159	0.678	0.621
0.6	"	0.0067	2.40	0.068	0.080	0.679	0.621
1.5	"	0.006	2.83	0.066	0.083	0.648	0.573
3.0	"	0.0058	3.46	0.047	0.055	0.679	0.623
10.0	"	0.0057	2.83	0.082	0.068	0.597	0.621
40.0	"	0.0094	1.39	0.101	0.107	0.710	0.679
—	alcohol	0.0085	1.21	0.096	0.140	0.748	0.650
0.2	"	0.009	1.21	0.135	0.159	0.678	0.621
0.6	"	0.0067	2.40	0.058	0.089	0.712	0.596
1.5	"	0.006	2.83	0.074	0.075	0.622	0.597
3.0	"	0.0058	3.46	0.054	0.055	0.648	0.623
10.0	"	0.057	2.83	0.074	0.075	0.622	0.597
40.0	"	0.0094	1.39	0.101	0.107	0.710	0.679

Note:

detailed particle size analysis see Appendix D

TABLE 3.16.

ORGANIC GRINDING OF CALCITE WITH VARYING ADDITIONS OF PROPIONIC ACID (MEAN VALUES).

addition of propionic acid (g/kg)	average oil of adsorption (g/m^2) before desorption	after desoption
--*)	0.106	0.110
0.2	0.136	0.147
0.6	0.072	0.074
1.5	0.078	0.075
3.0	0.058	0.053
10.0	0.074	0.075
40.0	0.136	0.104

*) blank

TABLE 3.17.

EFFECT OF SURFACE TREATMENT OF CALCITE AFTER STANDARD GRINDING AT DIFFERENT AGING TIMES (SURFACE TREATMENT WET IN STIRRED BEAKER FOR 30 MIN IN 100 ml H_2O, WITH 1g ADDITIVES AND 20g SAMPLE.

aging time (hrs)	additive	oil of adsorption linseed oil	motor oil	average	average difference to blank sample (%)	Packing Fraction (PF) linseed oil	motor oil
0.0	---------*)	0.100	0.106	0.103	0.0	0.740	0.711
0.0	propionic acid	0.077	0.084	0.081	-21.4	0.787	0.756
1.0	" "	0.123	0.098	0.111	+7.8	0.698	0.726
24.0	" "	0.107	0.112	0.110	+6.8	0.727	0.699

*) blank

TABLE 3.18.
ESTABLISH GRIND CONDITIONS OF MICA (PHLOGOPITE)

mill charge	wt % - 325 mesh for: 15 min grind	30 min grind	60 min grind
0.5	31.3	35.5	36.6
1.0	33.0	39.2	41.0
1.5	45.3	54.5	69.1

NOTES

1) Targeted particle size distribution of 50% passing 45 um (d_{50})

2) size distribution of head sample:
99.9% -20 mesh, 0.9% -65 mesh
moisture content: 0.0%

3) selected grinding conditions (based on regression analysis):
25 min grinding time
0.5 kg mineral charge
classifying to -100 mesh

4) detailed screen analyses in Appendix E

TABLE 3.19.
ORGANIC GRINDING AND CHARACTERIZATION OF PHLOGOPITE/MICA

additive	desorption media	calculated surface area	oil of adsorption (g/m^2) linseed oil	oil of adsorption (g/m^2) motor oil	flow point (g/m^2) linseed oil	flow point (g/m^2) motor oil	Packing Fraction (PF) linseed oil	Packing Fraction (PF) motor oil
-------*)	-----	1.2	0.218	0.220	0.516	0.561	0.559	0.535
-------	H_2O	"	0.252	0.213	0.543	0.603	0.523	0.543
-------	alcohol	"	0.233	0.213	0.479	0.568	0.543	0.543
propanol	-----	1.3	0.225	0.204	0.487	0.522	0.532	0.534
"	H_2O	"	0.232	0.213	0.572	0.606	0.524	0.523
"	alcohol	"	0.215	0.246	0.555	0.622	0.543	0.487
propionic acid	-----	1.6	0.171	0.181	0.430	0.434	0.548	0.512
" "	H_2O	"	0.189	0.186	0.393	0.466	0.523	0.505
" "	alcohol	"	0.160	0.133	0.451	0.479	0.565	0.588
ether	-----	0.9	0.306	0.303	0.708	0.753	0.547	0.527
"	H_2O	"	0.259	0.308	0.723	0.758	0.588	0.523
"	alcohol	"	0.232	0.284	0.672	0.733	0.614	0.543
ketone	-----	1.4	0.213	0.192	0.446	0.490	0.527	0.530
"	H_2O	"	0.183	0.198	0.515	0.517	0.565	0.523
"	alcohol	"	0.216	0.213	0.515	0.533	0.523	0.504
kerosene	-----	1.08	0.229	0.225	0.538	0.619	0.573	0.555
"	H_2O	"	0.280	0.276	0.732	0.651	0.523	0.505
"	alcohol	"	0.258	0.197	0.581	0.631	0.544	0.588

*) blank

NOTE:

detailed particle size analysis in Appendix E

TABLE 3.20.

ORGANIC GRINDING OF PHLOGOPITE/MICA
(MEAN VALUES AND SELECTED DATA)

organic additive	average oil of adsorption (g/m^2) before *) desorption	after **) desorption	initial relative adsorption number	d_{50} ****)	surface area (m^2/g)
---- ***)	0.219	0.228	1.01	24.0	1.20
propanol	0.215	0.227	0.904	22.5	1.30
propionic acid	0.176	0.167	1.06	21.0	1.60
ether	0.305	0.271	0.99	22.0	0.90
ketone	0.203	0.203	0.903	19.0	1.40
kerosene	0.227	0.253	0.984	23.0	1.08

*) mean of 2 values

**) mean of 4 values

***) blank

****) detailed particle size analyses in Appendix E

TABLE 3.21.

EFFECT OF SURFACE TREATMENT OF MICA (PHLOGOPITE) AFTER STANDARD GRINDING AT DIFFERENT AGING TIMES (SURFACE TREATMENT WET IN STIRRED BEAKER FOR 30 MIN IN 100 ml H_2O, WITH 1g ADDITIVES AND 20g SAMPLE.

aging time (hrs)	additive	oil of adsorption			average difference to blank sample (%)	Packing Fraction (PF)	
		linseed oil	motor oil	average		linseed oil	motor oil
0.0	——	0.155	0.178	0.167	0.0	0.641	0.587
0.0	propionic acid	0.202	0.170	0.186	+11.4	0.578	0.598
1.0	" "	0.233	0.228	0.231	+38.3	0.543	0.526
24.0	" "	0.233	0.242	0.238	+42.5	0.543	0.511

TABLE 3.22.

SELECTION FILLER, EVALUATION OF ORGANIC GRINDING RESULTS BASED ON MEAN OIL OF ADSORPTION VALUES (in g oil/m^2)

mineral	formula	chemical bondings	best additive	improvement after desorption (%) *)	overall improvement (%) **)
silica	SiO_2	covalent	propanol	+3.4	19.4
talc	$Mg_3 Si_4 O_{10} (OH)_2$	Van der Waals, covalent + ionic	propionic acid	0.0	35.0
calcite	$CaCO_3$	ionic	propionic acid	+8.6	48.6
mica/ phlogopite	$KMg_3 Si_3 AlO_{10} (F,OH)_2$	ionic + covalent	propionic acid	+5.1	23.3

*) $100 - 100 * \frac{\text{(oil of adsorption after desorption)}}{\text{(oil of adsorption before desorption)}}$

**) 100 -100 *(a/b)

a = average oil of adsorption values after organic grinding

b = average oil of adsorption values after blank grinding (before + after desorption)

TABLE 3.23.

FILLER PERFORMANCE COMPARISON OF TALC PRODUCTS FROM TEST PROGRAM WITH COMMERCIAL TALC FILLERS.

manufactorer	Trade Name	coated	surface area (m_2/g)	oil of adsorption ($g\ oil/m^2$) before desorption	oil of adsorption ($g\ oil/m^2$) after desorption	improvement (%) **)
-----	---- *)	no	4.82	0.059	0.060	--
-----	---- *)	yes	7.74	0.039	0.039	34.5
PFIZER	MP 10 -52	no	12.1	0.059	--	--
PFIZER	Micro Pflex 1200	yes	12.1***)	0.050	--	15.3
PFIZER	Microtuff 1000	yes	12.1	0.046	--	22.0

*) products from test program

**) see Table 3.22.

***) calculated from average particle size

TABLE 3.24.

FILLER PERFORMANCE COMPARISON OF CALCITE PRODUCTS FROM TEST PROGRAM WITH COMMERCIAL CALCITE FILLERS WITH AND WITHOUT SURFACE TREATMENT.

manufactorer	Trade Name	coated	surface area (m_2/g)	oil of adsorption ($g\ oil/m^2$) before desorption	oil of adsorption ($g\ oil/m^2$) after desorption	improvement (%) **)
---	---*)	no	1.21	0.106	0.110	--
---	---*)	yes	3.46	0.058	0.053	48.6
PLUESS-Stauffer	Verflake	no	2.5	0.065	--	--
" "	Verflake T	yes	2.5	0.031	0.044	42.3
PFIZER	Vicron 15-15	no	2.4	0.087	--	--
"	PFINYL 402	yes	2.5	0.047	0.060	38.5
"	HI-PFLEX 100	yes	3.5	0.039	--	55.2

*) products from test program
**) see Table 3.22.

FIG. 3.1. Organic grinding of silica, results for weight-related oil of adsorption values

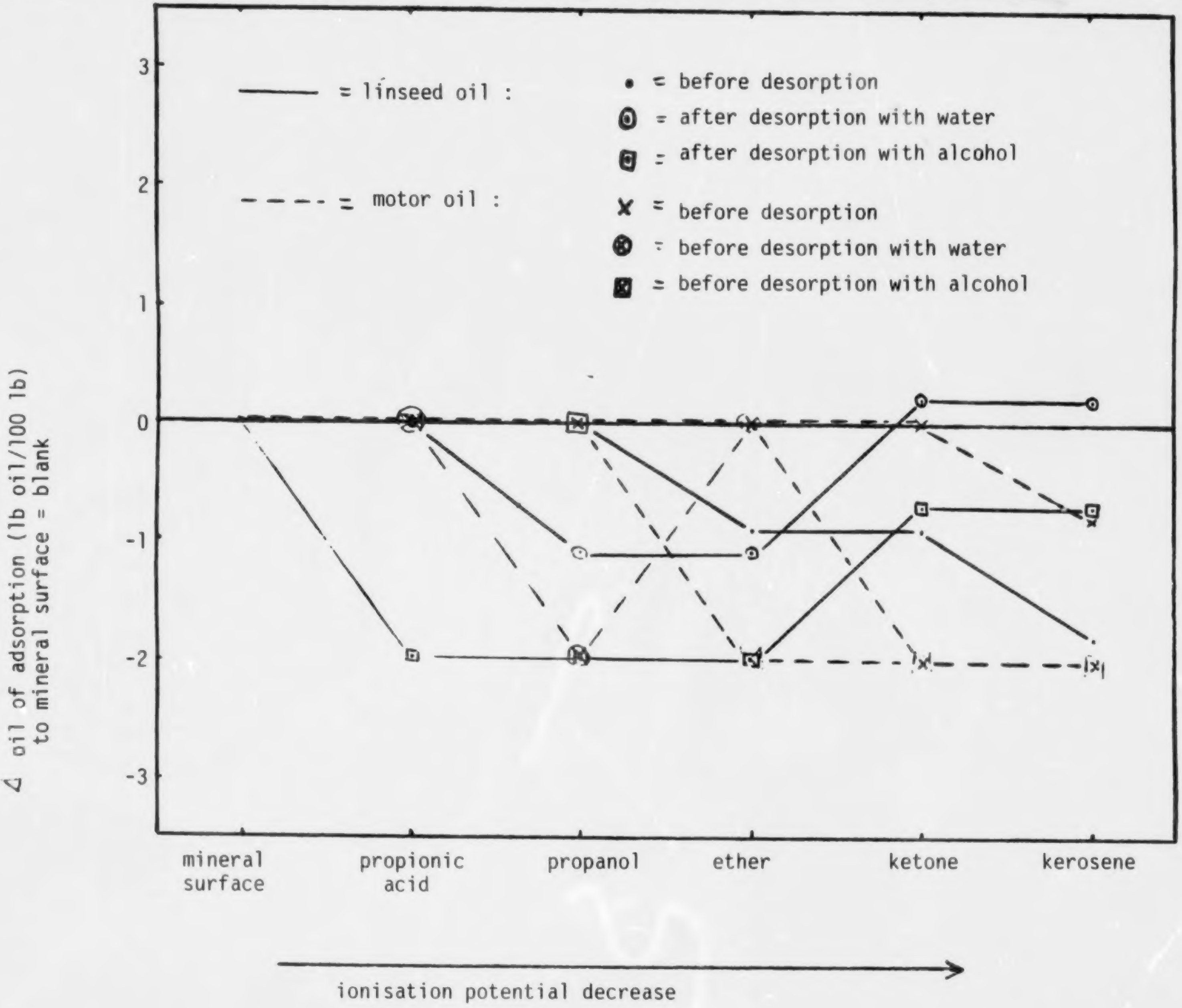


FIG. 3.2. Organic grinding of silica, results for surface-related oil of adsorption values

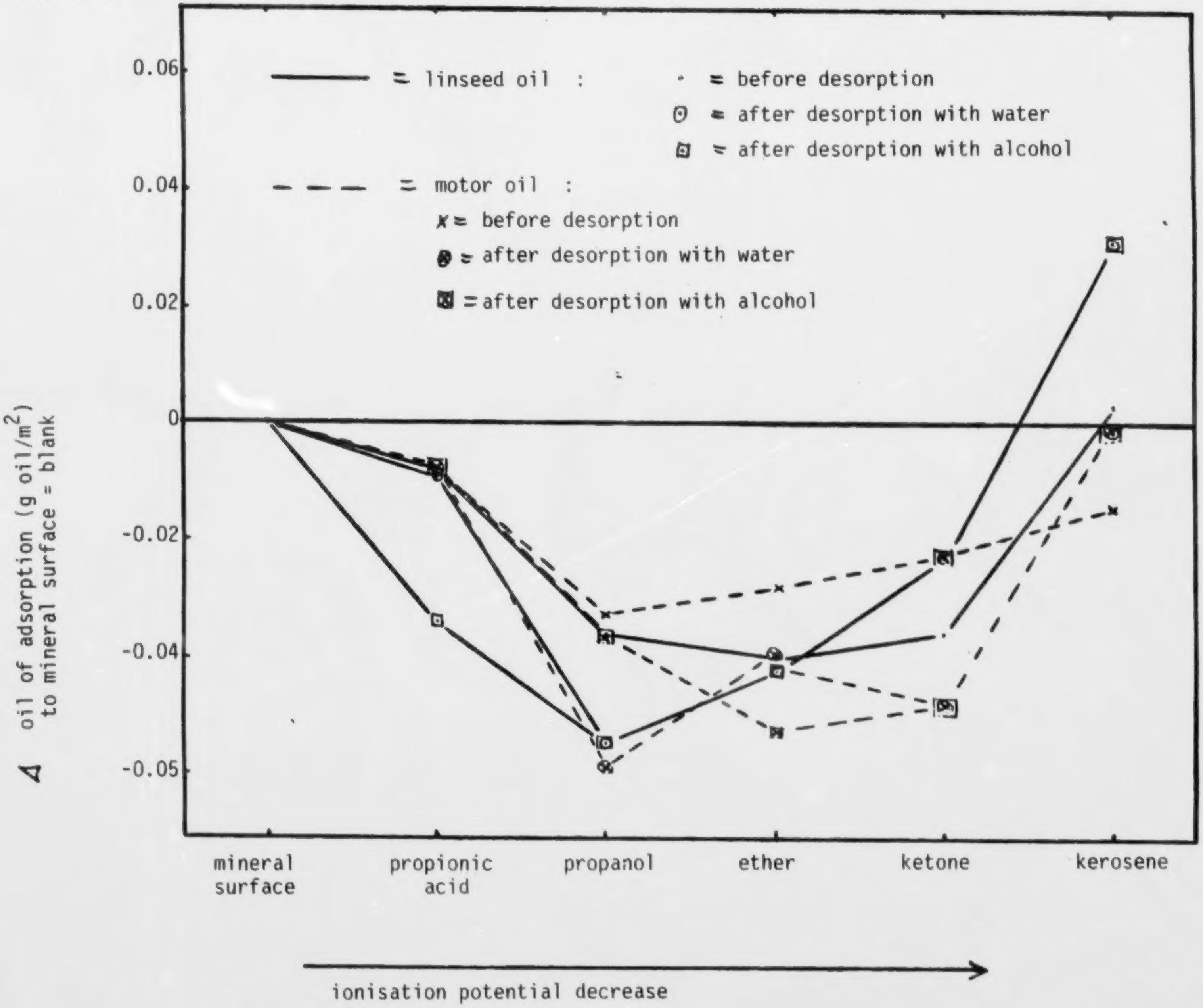


FIG. 3.3. Organic bonding of silica, results for weight-related Daniel flowpoint values

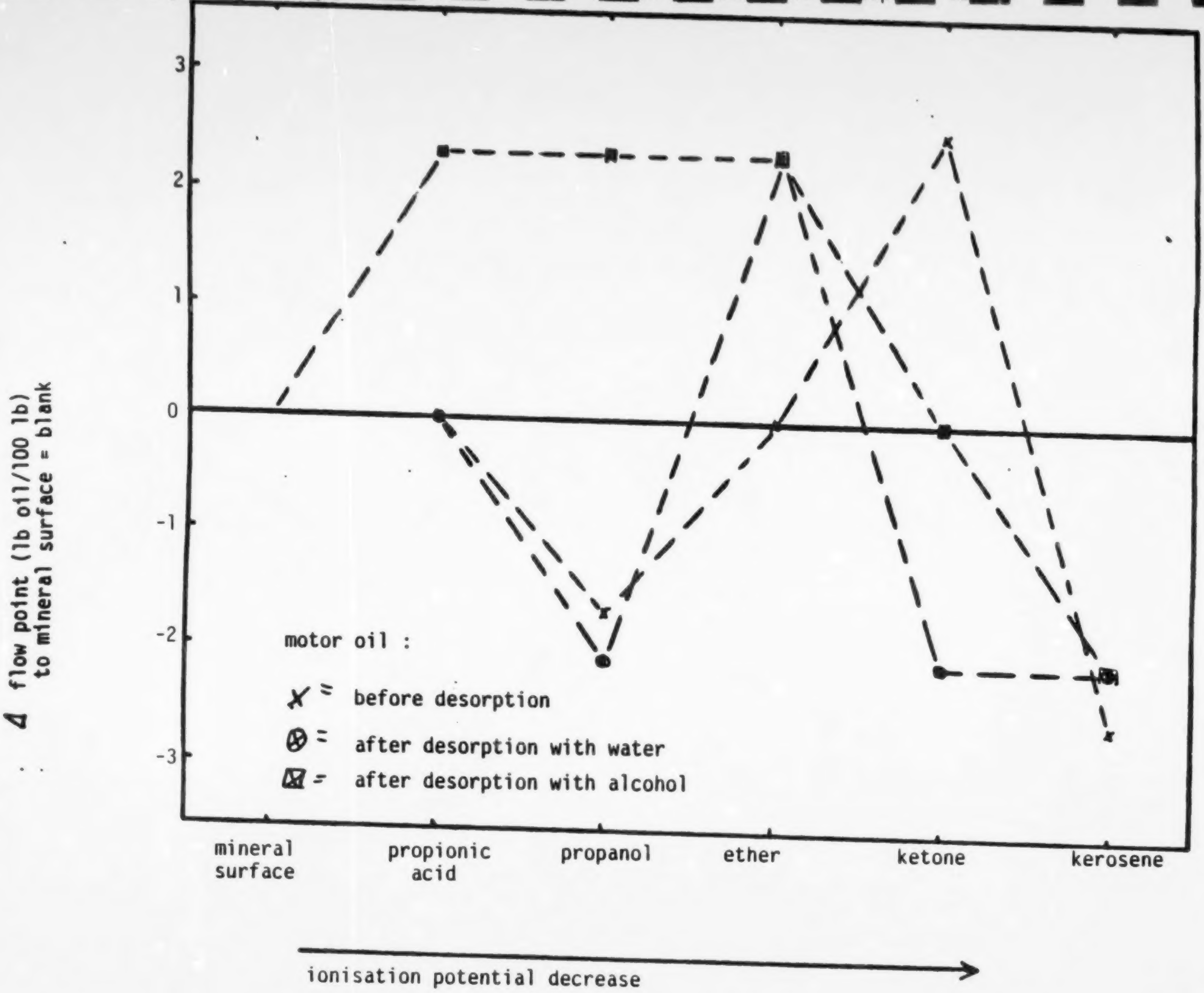
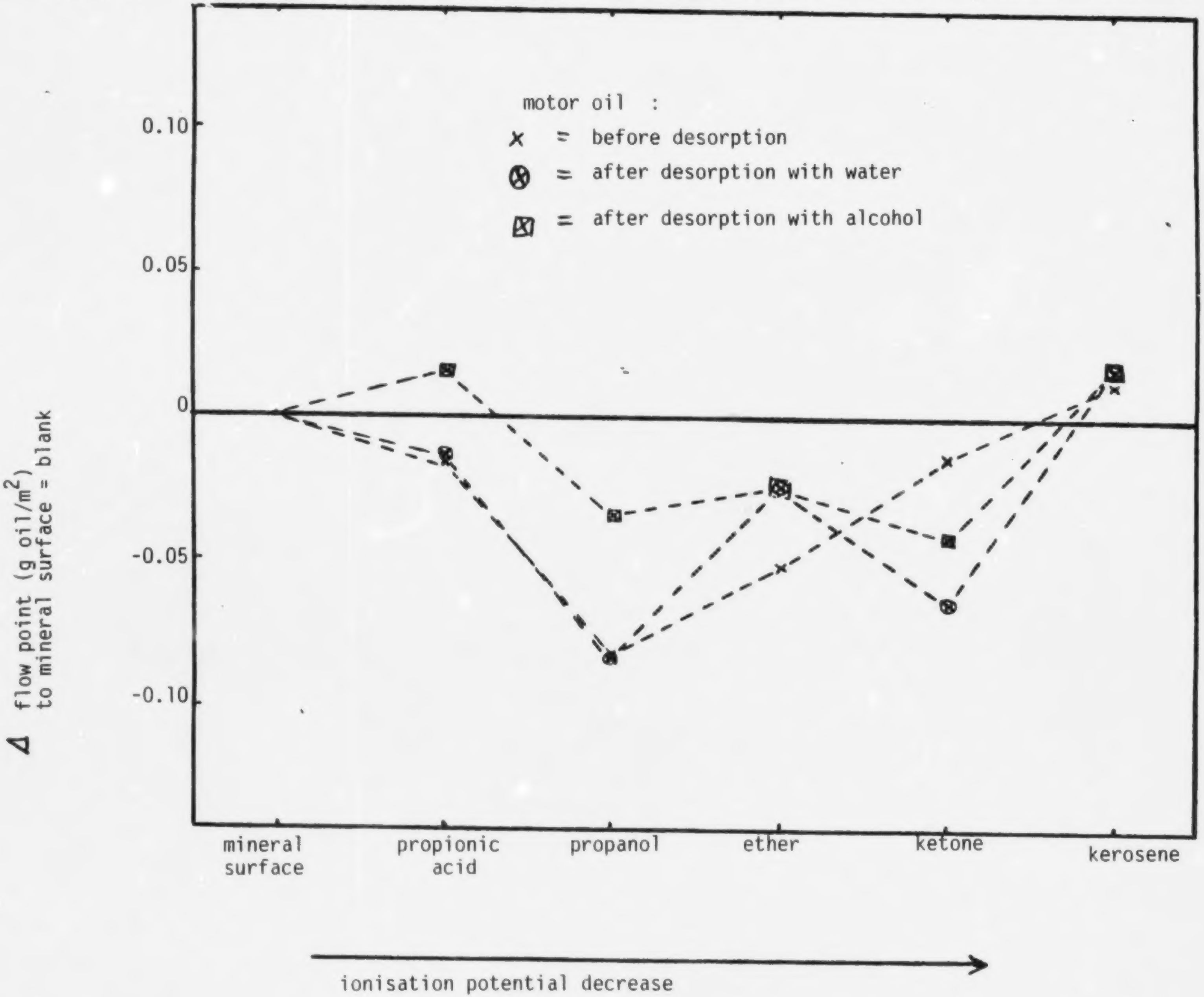


FIG. 3.4. Organic grinding of silica, results for surface-related Daniel flow point values



[redacted] FI[redacted].5.[redacted]Org[redacted] gr[redacted]ing[redacted]sil[redacted] re[redacted]ts [redacted]rel[redacted]ve a[redacted]rpt[redacted]num[redacted] and[redacted]rfa[redacted]ela[redacted] me[redacted]il [redacted] [redacted]
adsorption values.

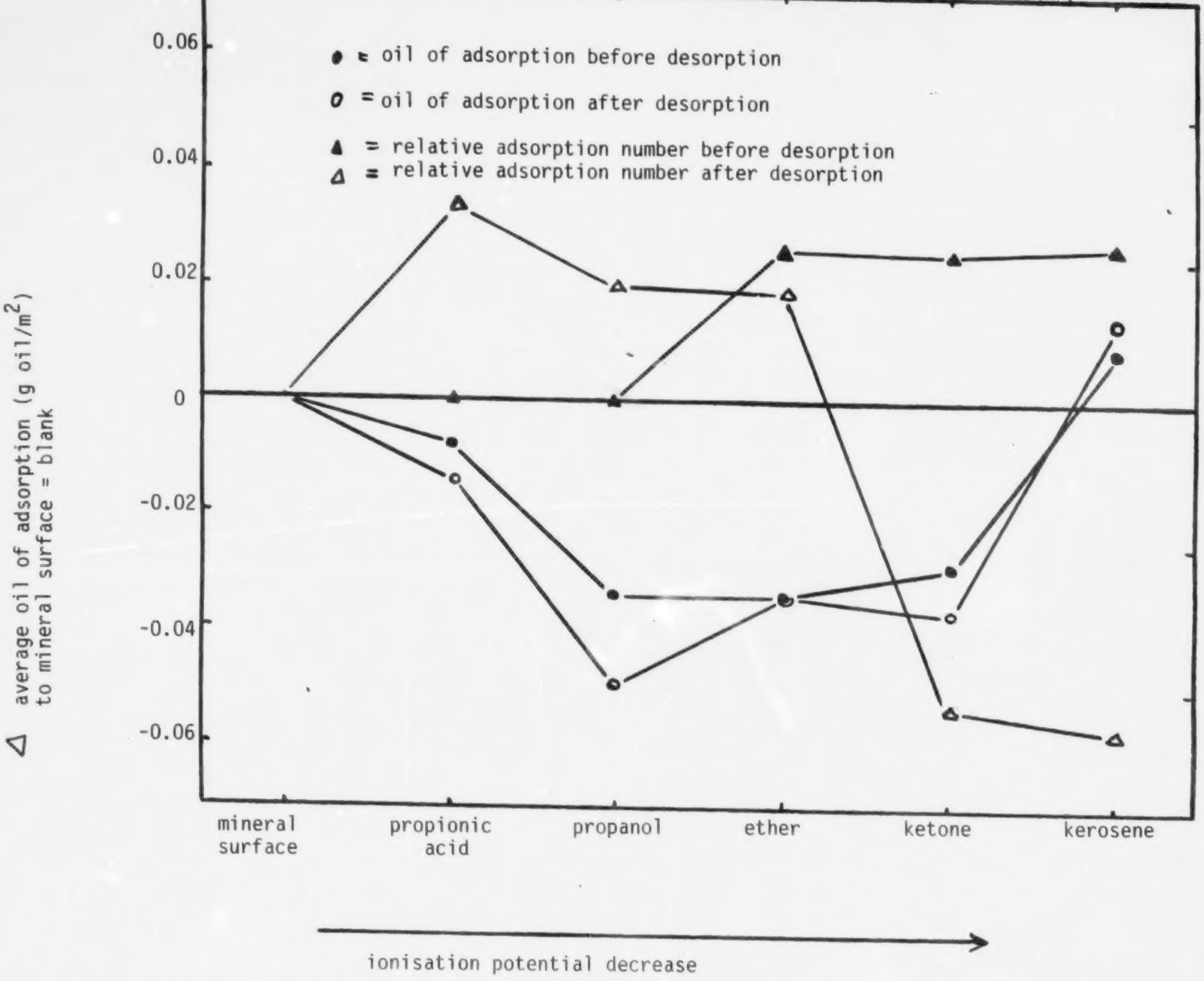


FIG. 3.6. Organic grinding of silica, influence of water content of mineral charge

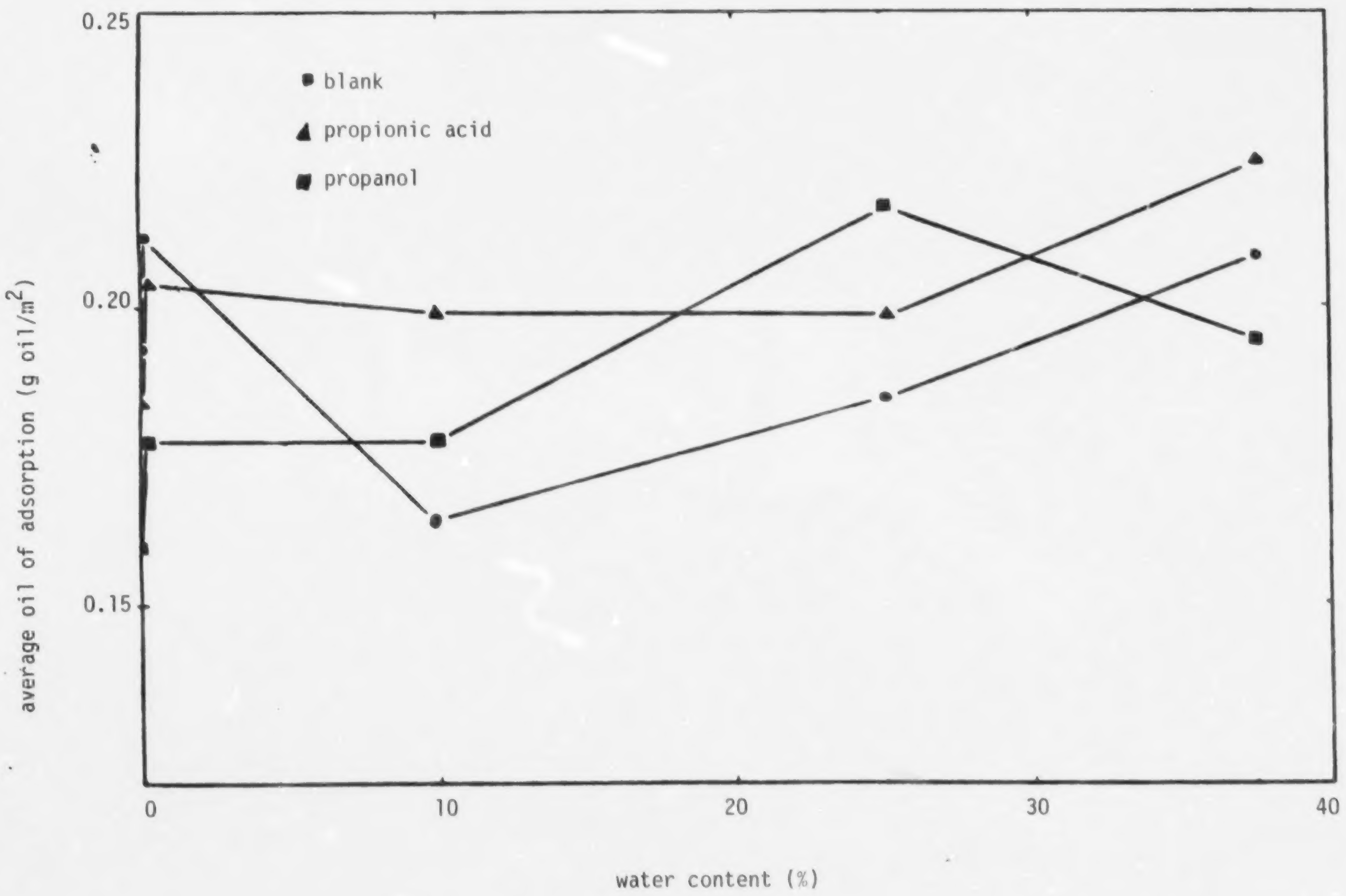


Fig. 3.[illegible] Organic grinding aid [illegible] results for surface related mean of oil adsorption values

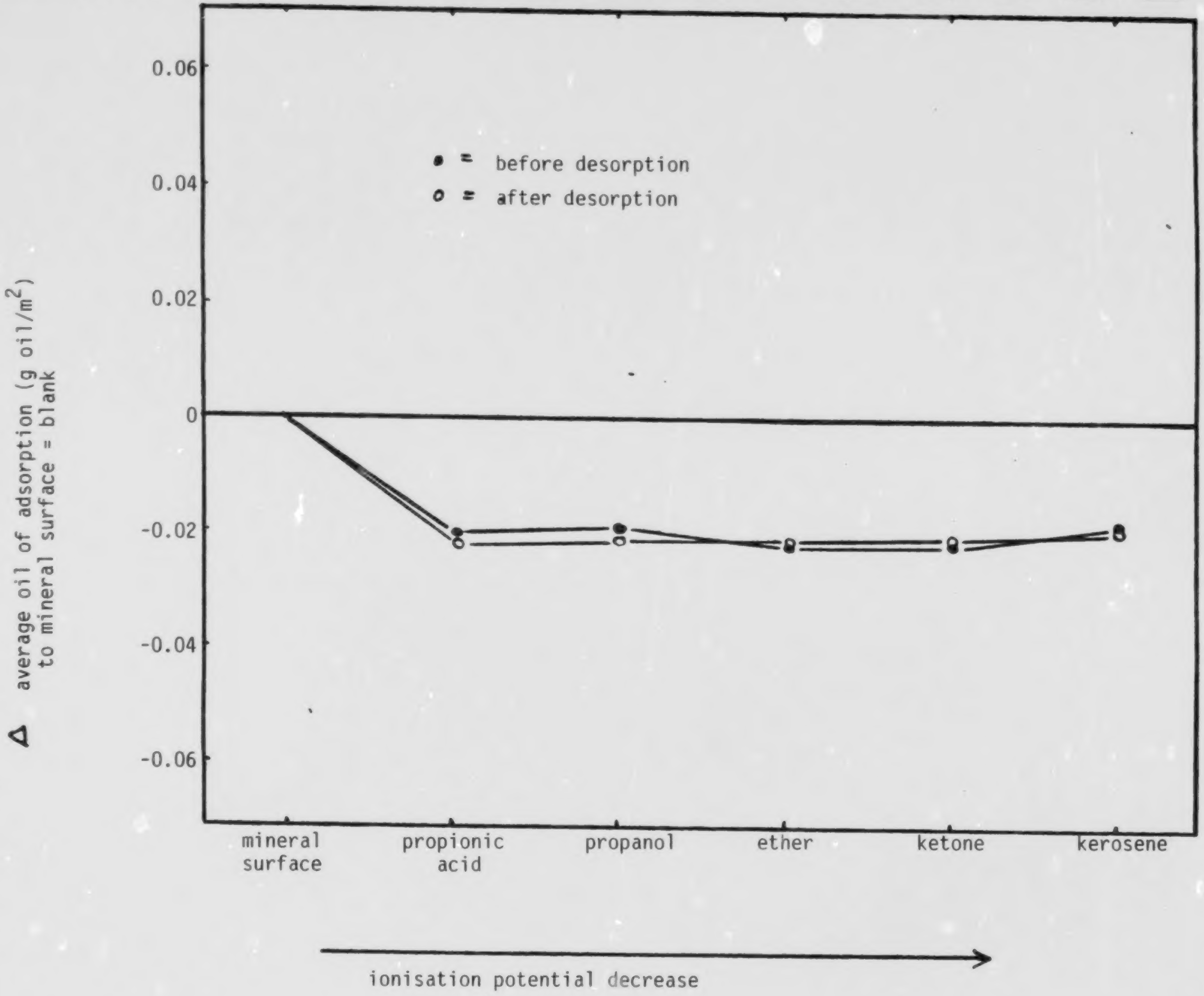


Fig. 3.9 Organic grinding of calcite results for surface related mean oil of adsorption values

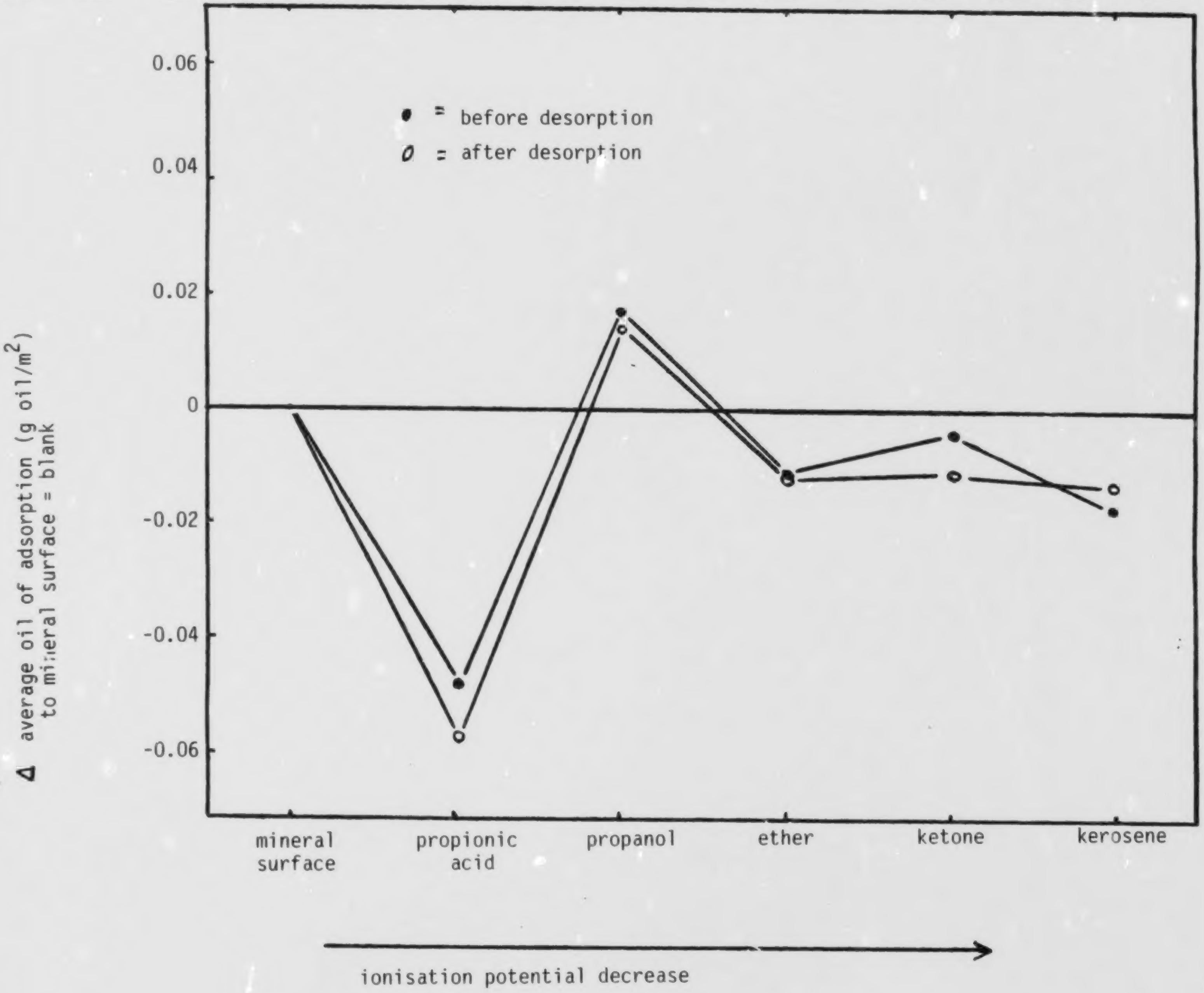


FIG. 3.9. Organic and blank grinding of calcite with varying water contents of mineral charge, influence on average surface related oil of adsorption.

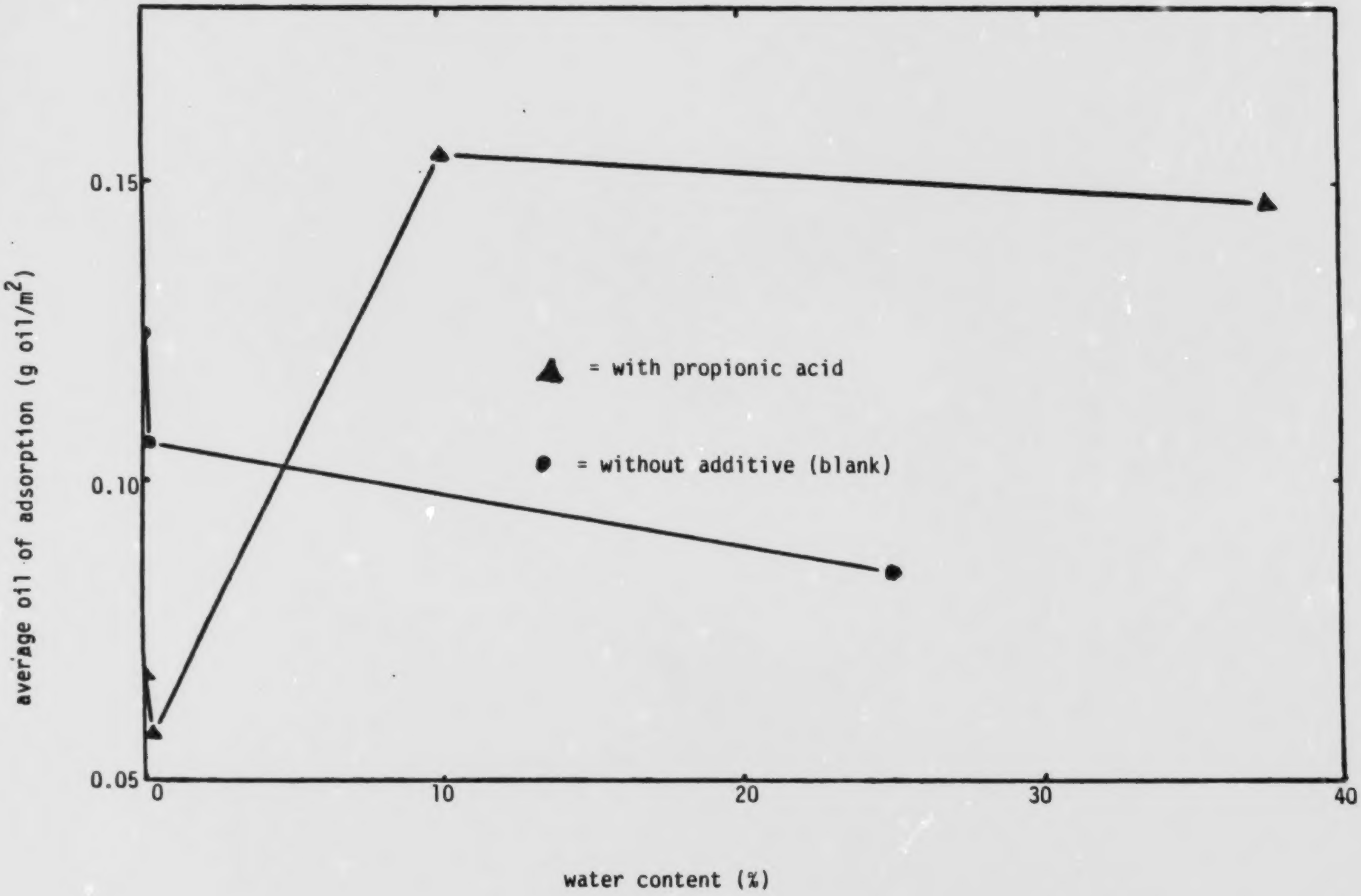


FIG. 3.10. Organic grinding of calcite with varying additions of propionic acid, influence on average oil of adsorption and difference (Δ) by desorption tests.

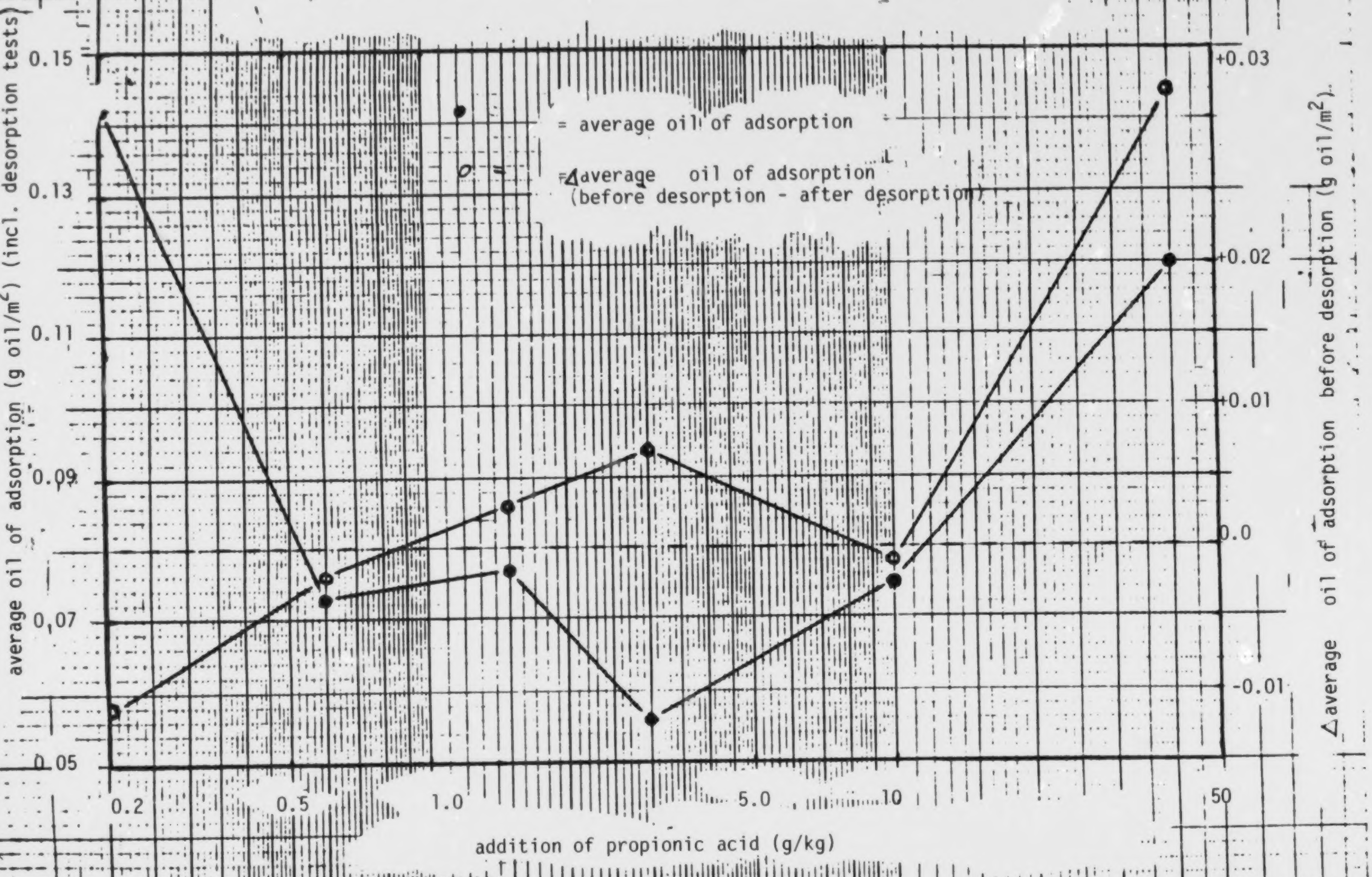
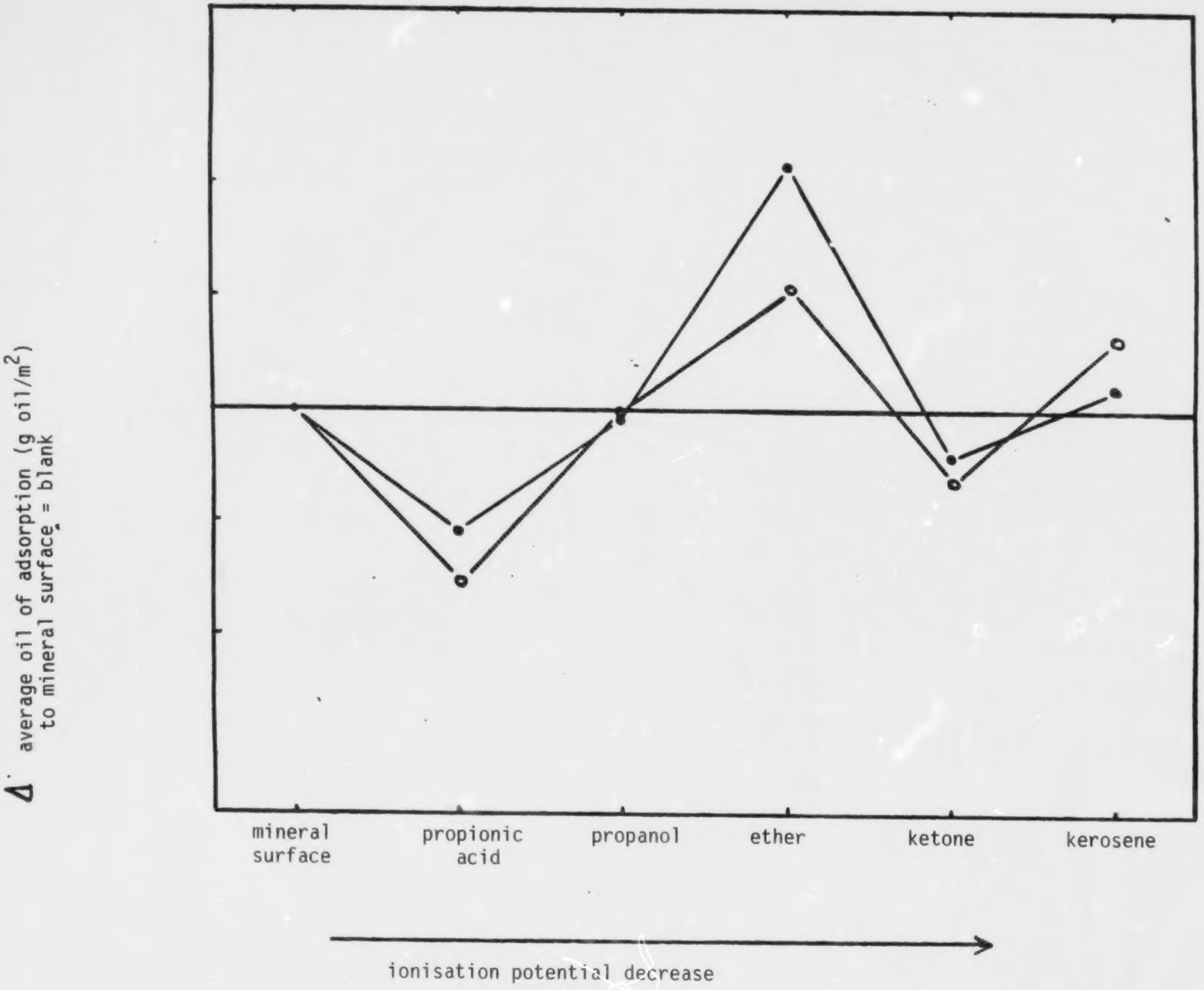


Fig. 3.11. Organic grinding of phlogopite, results for surface related mean oil of adsorption values



4. SUMMARY AND CONCLUSIONS

For all studied industrial minerals, improvement of the surface related oil of adsorption values was achieved by dry grinding with the either propionic acid or propanol. The oil of adsorption value was chosen as parameter to evaluate the potential of the ground products as a plastic filler. When related to the surface area of a given ground product, the oil of adsorption value indicates the wetability and dispersion behaviour of the product in nonpolymerized plastic resins. The basis of evaluation is the simple comparison to the blank ground sample for each mineral. An alternative to the oil of adsorption is given by the determination of the Daniel flow point. However, this method was found to be less accurate. The validity of the oil of adsorption value as plastic filler evaluation parameter was shown in an earlier publication by FERRIGNO (1982) and is employed by ASTM standards.

Mechanochemical grinding of calcite, phlogopite (Mg-Mica) and talc with propionic acid as well as silica with propanol rendered products of improved (decreased) oil of adsorption values. A further improvement was noticed for these mineral filler additive combinations after desorption tests. These tests point out that stable organic surface coatings were present. This indicates further economical improvements by adjusting the addition rate of propionic acid or propanol at an even lower level. In spite of the fact that the chosen standard additions of organics were three times lower than in conventional surface modification, a further possible three fold drop of propionic acid addition in to the calcite grinding stage was established by the test work.

The low or reversed effectiveness of the additives di-isopropylether, methyl isopropyl ketone and kerosene can be explained by their lower ionization potential; which provides less stable chemical bondings. Another reason for adverse effects of the ether and ketone might be given by their ability to react amphotericly, which can also cause hydrophilic instead of organophylic behaviour.

Wet surface modification with the tested organic additives after dry blank grinding caused decreased oil absorption values only for talc and calcite, when applied immediately after the grinding stage. After aging for 1 hr and 24 hrs the oil uptake was increased when compared the blank sample. Increased oil absorption values were also observed after wet grinding with organic additives. Therefore it can be concluded that surface hydration is responsible for inhibited or hampered surface modification with organic additives of low molecular weight.

The potential of the best test ground products to serve as surface modified plastic fillers was proven for calcite and talc (ground with propionic acid) by comparing their surface related oil absorption behaviour with that of comprehensive commercial grade fillers. Attempts to detect the nature of the bonding of the organic additives to the minerals surface by infrared spectometry and by DTG failed due to the fact that the organic additive amounts were in all cases below the detection limits.

The findings lead to the conclusion that the best perspectives for mechanochemical surface treatment are connected to dry ginding a filler mineral with ionic bondings and an organic additive with a relatively high ionization potential (dielectric constant) and one reactive group. The most promising result was given by the combination of calcite as filler and propionic acid as additive.

The low consumption (3 kg/t = 0.3%) and the low prices of the proposed organic grinding additives lead to the following comparison, which is based on bulk prices:

surface modifying reagent:	reagent costs/ton mineral fillers:	
isopropanol	2.62	CDN $
propionic acid	4.35	"
sodium stearate *)	35.8	"
stearic acid *)	13.5	"
silicone polyalkoxylate *)	78.5	"
cocamino propionic acid *)	37.5	"

*) estimated additive consumption 1%

The economic advantages of propionic acid and isopropanol are obvious, since it is expected that the prices of the ground products are comparable to comprehensive traditionally surface modified commercial fillers. Technical problems in the dry mechanochemical grinding stage due to fumes of isopropanol or propionic acid are not very likely. Fume formations can easily be controlled by minor modifications of the dust controlling measures.

5. RECOMMENDATIONS

The described test results suggest that the mechanochemical surface modification of industrial fillers with inexpensive organic solvents is a technique with potential merit. For further evidence and commercial development the following is recommended:

- Prepare batches of each mineral using the most suitable organic reagent and evaluate their performance in various polymer resins. The resins should include: PVC, Polypropylene, Polyester and Nylon.

- Seek industrial partner(s) to further the development work on a pilot scale.

G. Heinrich	Craig A Booth
G. Heinrich Project Scientist Mineral Resources	C.A. Booth Project Scientist Mineral Resources
V.I. Lakshmanan	G.M. Freeman
V.I. Lakshmanan Project Manager Mineral Resources	G.M. Freeman Operations Manager Mineral Resources

Supply and Services Canada

TABLE 6.1.

CONTRACT PLAN AND REPORT FORM — [illegible]

CONTRACT TITLE — TITRE DU CONTRAT MECHANOCHEMICAL GRINDING OF INDUSTRIAL MINERALS

CONTRACTOR — ENTREPRENEUR ONTARIO RESEARCH FOUNDATION

1450. 23440-7-9177

[illegible]	1 Nov.	2 Dec.	3 Jan.	4 Feb.	5 March	6	7	8	9	10	11	12	[illegible]	[illegible]	[illegible]
Establish Grind Time													$ 7,390	7,500	- 11
Organic Grinding													$16,710	16,000	+ 11
Product Characterization													$15,950	23,196	-724
Polymer/Filler Performance													$ 8,020	6,380	+164
Data Analysis													$ 9,000	9,000	
Reporting													$ 9,000	9,000	
													PLAN $66,070		
[illegible]	9,669	11,025	16,912	19,464	9,000									[illegible]	[illegible]
% [illegible]	4,383	11,266	19,555	30,655	5,817									71,676	5.6

7. LITERATURE

1) HASKIN, R.W. & ECKERT, Minerals in plastics - Meeting the challenge of the future; Industrial Minerals (March 1987) p.54-59

2) DICKSON, T: US plastics - A growing mineral market; Industrial Minerals (Feb 1987) p.50-57.

3) HARRIS, T.S.: Overview of the Chemically Modified Mineral Marketplace and Technology; Chemically Modified Mineral Conference, Toronto, Ontario (Oct. 8-9, 1986).

4) BENSOW, R.E. & CASTLE, T.E.: Reactions of Freshly formed surfaces of silicas; I. Phys. Chem., 62 (1958) p.840.

5) BALLARD, C.C. pt al: Esterification of the Surface of Amorphous Silica, I. Phys. Chem., 65 (1961) p.20.

6) ASTM - standard D 281: 'Test Method for Oil Absorption of Pigments by Spatula Rub-Out".

7) ASTM - standard D 1755: 'Standard Specification for Poly (vinyl Chloride) Resins'.

8) FERRIGNO, T.H.: 'Oil of adsorption: Refining an ancient art', Plastics Compounding (Nov./Dec. 1982) p. 21-26.

9) PFIZER MINERALS, PIGMENT & METALS DIV.: 'PFINYL 402 - TECHNICAL DATA, spec. sheet No TR-301-1 (1980) p. 1-3.

10) DANIEL, F.K.: 'A System for Determining the Optimum Grinding Composition of Paints in Ball and Pebble Mills, Scientific

Section - National Paint, Varnish and Lacquer Ass. Inc. (Oct. 1950) p. 386-406.

11) YOUNG, R.P.: 'Reinforced Molding Compounds, in LUBIN, G. : 'Handbook of Fiberglass and Advanced Plastic Composits', Polymer Technolgy Series, New York (1969) p. 396, 893 pages.

APPENDICES

APPENDIX A

CALCULATION PROCEDURES,
SELECTED LITERATURE.

REGRESSION ANALYSIS

y, x = interdependant variables like d_{50} (particle size at 50% passing imaginable screen), grinding time, mill load with sample material

b, m = constants of resulting equation:
$y = m*x + b$ (linear regression)
$\ln y = m*n\ x + b$ (exponentiel regression)
and $y = EXP(m*\ln x + b$

linear regression:

$m = ((n\ \ xi * Yi)1 - (\ xi.\ Yi))/((n\ \ xi^2) - (\ \ xi)^2\ ))$
$b = (\ Yi - m.\ \ Xi)/n$

expontential regression:

like linear regression, but with x = ln x and y = ln y

example: calibration grinding of talc (0.5 kg charge)

d50 = x (um)	grind time = y (min)
15	15
12.5	30
8.3	60

$$m = \frac{(3.(15.15+12.5.30+8.3.60))-(15+12.5+8.3).(15+30+60))/)}{(3x(15^2+12.5^2+8.3^2))-(15+12.5+8.3)^2)/3)} = 6.76$$

$$b = ((15+30+60)+6.76(15+12.5+8.3))/3 = 115.7$$

A regression analysis method was used to determine the optimum grinding conditions (grind time and mill charge). A brief description of the method along with an sxample is presented below.

OIL OF ADSORPTION & FLOW POINT CALCULATION

$$\frac{100.\ \text{used oil volume (ml). Specific oil density (9/cm3)}}{\text{used sample mass (g)}}$$

oil of adsorption or flow point (g^{oil}/100 g sample)

example: oil of adsoprtion of talc sample after grinding of 500 g for 75 min without additives

$$\frac{100.\ 3.1\ \text{ml}*0.93\ (\text{g/cm3})}{10.12\ \text{g}} = \underline{28.5} \qquad (\underline{\text{g linseed oil}})$$

adsorption behavior:

relative adsorption number =

$$\frac{\text{oil of adsorption for non-polar oil (goil/100sample)}}{\text{oil of adsorption for (polar) linseed oil } (\text{g}^{\text{oil}}/100\text{g sample})}$$

*) motor oil (half synthetic) was used as model substance

example: relative adsorption number for silica sample after grinding of 750g for 90 min. without additives.

$$\frac{15.3\ (\text{g motor oil/100 g sample}) =}{16.7\ (\text{g}^{\text{linseed oil}}/100\text{ g sample})} \qquad \underline{0.916} \qquad \frac{(\text{g motor oil})}{\text{g linseed oil}}$$

Oil of Adsorption:

Procedure:

The procedure to determine the oil adsorption relies upon ASTM standard D-281 and comprises the following steps:

1) 50 to 10 g sample (depending upon specific gravity) of the product to be tested is placed in a petri-dish.

2) A burette containing linseed (or motor oil) of known specific density is positioned above the petri-dish with the initial oil volume in the burette.

3) The oil is gradually (dropwise) added and rubbed into the sample with a spatula until the oil-sample mixture becomes stiff and putty-like and starts to stick to the spatula.

4) The final oil volume in the burette is measured.

The amount of oil required is derived from the oil volume (initial volume in burette minus final volume in burette), by multiplication with the specific density of the oil.

2. Meaning of the Oil Absorption Values

In general, the oil absorption value of a powder sample is the amount of (linseed) oil that is absorbed by the powder sample to form a stiff putty. In other words, it is the minimum amount of oil required to cover, or "wet" each particle. It is dependant on the specific surface of the sample and its wetability by organic fluids. High surface areas cause a high oil absorption value, whereas the oil absorption value decreases with increased wetability by organic fluids. This means that the oil absorption value allows pre-estimates of either the specific surface of a sample or its dispersion behaviour in organic resins for paints and plastics. The lower the oil absorption value is for a given specific surface area, the better is the dispersion behaviour of the sample in organic resins. Such improved dispersion behaviour of mineral filler materials allowsthe manufacture of paints and plastics with a higher filler or pigment loading.

Designation: D 281 – 31 (Reapproved 1980)

An American National S

Standard Test Method for
OIL ABSORPTION OF PIGMENTS BY SPATULA RUB-OUT[1]

This standard is issued under the fixed designation D 281; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This method has been approved for use by agencies of the Department of Defense to replace Method 4191 of Fed. Test Method Standard No. 141A and for listing in the DoD Index of Specifications and Standards.

Scope

1.1 This method covers a procedure for determining the oil absorption of pigments by spatula rub-out.

2. Procedure

2.1 Weigh exactly 1 g, or any multiple thereof (Note 1), of the thoroughly mixed and air-dried pigment, and place upon a glass plate or marble slab. Weigh accurately a dropping bottle (Note 2) fitted with a ground-in pipet and rubber bulb and containing some clear, well-settled, raw linseed oil (free from foots) having an acid value (Note 3) of from [illegible] to 3 (Note 4). Add the linseed oil gradually, drop by drop (by means of the pipet) to the pigment, and after the addition of each drop thoroughly incorporate the oil with the pigment by rubbing up with a sharp-edged steel spatula. The test is complete when exactly enough oil has been incorporated with the pigment to produce a very stiff, putty-like paste, which does not break or separate. Accurately weigh the bottle and oil (Note 2) and determine by difference the weight of oil used.

NOTE 1—The weight of sample depends upon the specific gravity, fineness, and other characteristics of the pigment. For example, if 20 g is taken for white lead, about 1 g is sufficient for carbon black. In any event the size of sample should be large enough so that at least 1 g of oil is required.

NOTE 2—Instead of weighing the linseed oil in the dropping bottle, it may be added drop by drop from an accurate buret. The number of milliliters of linseed oil used is then multiplied by the specific gravity of the oil in order to obtain the corresponding weight of the oil in grams.

NOTE 3—Care should be taken that the linseed oil used in comparative or simultaneous tests has the same acid value.

NOTE 4—While raw linseed oil is specified, other liquids (such as refined oil) may be used by mutual agreement.

3. Calculation

3.1 From the weights of oil and pigment used in the test, calculate the number of pounds of oil required to exactly "wet" 100 lb of pigment.

---

[1] This method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings and Materials.

Current edition accepted Sept. 1, 1931. Originally issued 1928. Replaces D 281 – 28 T.

The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, Pa. 19103.

Designation: D 283 – 52 (Reappr

Standard Methods of
CHEMICAL ANALYSIS C COPPER PIGMENTS[1]

This standard is issued under the fixed designation D 28 year of original adoption or, in the case of revision, the ye reapproval.

These methods have been approved for use by agencies of Method Standard No. 141A and for listing in the DoD Ind

ε Note 1—Editorial changes in Section 16 and equation

ε Note 2—Sections 2, 4, and 5 were editorially added in

1. Scope

1.1 These methods cover procedures the chemical analysis of dry cuprous ox and copper pigments.

1.2 The analytical procedures appear the following order:

	Sectio
Total Copper	6
Total Reducing Power as Cuprous Oxide	7 and
Metallic Copper	9 and
Cuprous Oxide	11
Cupric Oxide	12
Metals Other than Copper	13 to
Chlorides and Sulfates	16 and
Acetone-Soluble Matter	18
Water	19
Stability	20
Coarse Particles	21
Coarse Particles Insoluble in Nitric Acid	22

2. Applicable Documents

2.1 *ASTM Standards:*

D 185 Test for Coarse Particles in ments, Pastes, and Paints[2]

D 1193 Specification for Reagent W

D 1208 Tests for Common Properti Certain Pigments[2]

3. Treatment of Sample

3.1 Grind dry pigments, if lumpy or finely ground, to a fine powder and oughly mix (Note 1). Large samples m thoroughly mixed and a representative tion taken and powdered if lumpy o finely ground. In all cases thoroughly m

ther wrinkled nor stretched, and place in instrument in the desired posi- red nd normal to the light beam.
djust the receptor position so that a va e is indicated or recorded. If sin use the specimen must also be rotated plane to a maximum value of trans- ht. Note the reading (I_t).
pea with other specimens or other po- sp men as desired.

ulation

al ate the specular transmittance, T_s, s:

$$T_s = 100 I_t / I_o$$

ht tensity with the specimen in the am, and
ght intensity with no specimen in the ear

5 No calculation is needed if I_o is set r a conversion chart or special scale is used t the instrument reading.

epo

The report shall include the following

1.1 ample designation,
1.2 nstrument used,
1.3 Average specular transmittance,
1.4 Number of specimens tested,
1. Standard deviation, and
1. Any measured anisotropy.

ting the validity of any patent rights asserted in ssl dvised that determination of the validity of ow esponsibility.

nical committee and must be reviewed every five ited either for revision of this standard or for en will receive careful consideration at a me ou omments have not received a fair hearing ace St., Philadelphia, PA 19103.

Designation: D 1755 - 81

Standard Specification for POLY(VINYL CHLORIDE) RESINS[1]

This standard is issued under the fixed designation D 1755; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This specification covers the establish- ment of requirements for homopolymers of vinyl chloride in original powder form intended for subsequent mixing and processing in ther- moplastic compositions. These resins have a nominal specific gravity of 1.4 and a theoretical chlorine content of 56.8 %.

NOTE 1—The chlorine content of a resin may be termined by Method D 1303.

1.2 Two types of resin have been recognized, eral purpose and dispersion. When mixed h the customary amount of plasticizer, gen- l-purpose resins yield a dry or moist powder dispersion resins yield a liquid slurry. many resins are polymerized to meet cial requirements, a system of classification been provided that permits a wide choice rades.[2]

The values stated in SI units are to be ded as the standard.

licable Documents

ASTM Standards:
02 Methods of Sampling and Testing Un- ated Paper Used for Electrical Insulation[3]
Test Method for Oil Absorption of Pig- nts by Spatula Rub-Out[4]
125 Test Methods for Electrical Conduc- ty and Resistivity of Water[5]
3 Test Method for Dilute Solution Vis- y of Vinyl Chloride Polymers[6]
Specification for Octyl Ortho-Phthal- ter Plasticizers[6]
Test Method for Total Chlorine in Chloride Polymers and Copolymers[7]
Method for Particle Size Analysis of ed Polymers and Copolymers of Vi- loride[8]
Test Method for Apparent Viscosity of Plastisols and Organosols at High Shear Rates by Extrusion Viscometer[8]
D 1824 Test Method for Apparent Viscosity of Plastisols and Organosols at Low Shear Rates by Brookfield Viscometer[8]
D 1895 Test Methods for Apparent Density, Bulk Factor, and Pourability of Plastic Materials[8]
D 1898 Practice for Sampling of Plastics[8]
D 1921 Test Methods for Particle Size (Sieve Analysis) of Plastic Materials[8]
D 2396 Test Method for Powder-Mix Time of Poly(Vinyl Chloride) (PVC) Resins Using a Torque Rheometer[8]
D 2873 Test Method for Interior Porosity of Poly(Vinyl Chloride) (PVC) Resins by Mercury Intrusion Porosimetry[8]
D 3030 Test Method for Volatile Matter (Including Water) of Vinyl Chloride Resins[8]
D 3892 Practice for Packaging/Packing of Plastics[9]
E 1 Specifications for ASTM Thermometers[10]

3. Classification

3.1 *Types*—This specification covers two types of resin:

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[1] This specification is under the jurisdiction of ASTM Committee D-20 on Plastics and is the direct responsibility of Subcommittee D20.15 on Thermoplastic Materials (Section D20.15.08).

Current edition approved June 26, 1981. Published October 1981. Originally published as D 1755 – 60 T. Last previous edition D 1755 – 78.

[2] Hutson, J. L., "Proposed Method for Classifying Poly(Vinyl Chloride) Resins", ASTM Research Report File No. RR: D-20-1: (May 20, 1959). Available on loan from ASTM Headquarters.

[3] *Annual Book of ASTM Standards*, Vols 10.01 and 15.09.

[4] *Annual Book of ASTM Standards*, Vol 06.02.

[5] *Annual Book of ASTM Standards*, Vol 11.01.

[6] *Annual Book of ASTM Standards*, Vol 08.01.

[7] Discontinued, see 1985 *Annual Book of ASTM Standards*, Vol 08.01.

[8] *Annual Book of ASTM Standards*, Vol 08.02.

[9] *Annual Book of ASTM Standards*, Vol 08.03.

[10] *Annual Book of ASTM Standards*, Vol 14.01.

3.1.1 *Type GP*—General-purpose resins primarily intended for either dry blending, preblending, or thermoplastic processing.

3.2.1 *Type D*—Dispersion resins primarily intended for use in organosols and plastisols. As a class, these are small in particle size.

3.2 *Grades*—This specification provides for as many grades of resin as may be selected from the possible combinations of requirements in Tables 1 and 4. A grade is designated by first indicating the type (GP or D), followed by cell numbers for each property in the order in which they are listed in Tables 1 and 4. Where there is no interest in a property, a "0" is entered in place of a cell number. Should it be desirable, a cell limit may be extended by half the cell range into the next higher or lower cell, but not both. When this is done, it is indicated by a dash above the cell number ($\bar{n}$) if the extension is into the higher cell, or a dash below ($\underline{n}$) if into the lower cell. Extension of cell limits applies only to cells where ranges of properties are allowed and not where maximum or minimum values are specified. The cell number of the first property (dilute solution viscosity) is separated from those that follow by a dash.

NOTE 2—Resin GP6-$\bar{4}$30$\underline{5}$4. This is a grade of general-purpose resin (see Table 1) having the requirements given in Table 2.[11] Standard values defined by round-robin testing of eight laboratories are listed in Table 3.

4. General Requirements

4.1 The resin shall be in powder form.

4.2 The resin shall conform to the requirements of Table 1 or 4 as specified by the type and grade designation agreed upon between the purchaser and the supplier.

NOTE 3—Properties not covered, such as heat stability, color, and volatile loss, may also be important for application performance in compounds.

5. Sampling

5.1 Unless otherwise agreed upon between the purchaser and the supplier, the material shall be sampled in accordance with the sampling procedure in Practice D 1898.

6. Number of Tests

6.1 One set of test specimens as prescribed in Sections 8 to 15 shall be considered sufficient for testing each batch.

7. Retest and Rejection

7.1 If any failure occurs, the be retested to establish confor ance with an agreement between and the supplier.

8. Packaging and Marking

8.1 *Packaging*—The material aged in standard commercial constructed as to ensure acceptance or other carriers for safe transp lowest rate to the point of otherwise specified in the contract

8.2 *Marking*—Unless otherwise between the purchaser and the ping containers shall be marked of the material, type and grade quantity contained therein, and the contract or order under which is made, the name of the supp number of the contract or order.

8.3 All packing, packaging, provisions of Practice D 3892 shall specification.

TEST METHODS

9. Dilute Solution Viscosity

9.1 Method D 1243.

10. Apparent (Bulk) Density

10.1 Methods D 1895.

11. Sieve Analysis

11.1 Method D 1921.

NOTE 4—Method D 1705 may be the option of the purchaser and the

NOTE 5—Specifications for sieve 1) are primarily intended to control

12. Brookfield Viscosity

12.1 Method D 1824. Take rea Brookfield RVF viscometer at 20 No. 6 spindle. Prepare the plasti follows:

12.1.1 *Plasticizer*—Di (2-ethyl ate (DOP), Type I in Specificatio

12.1.2 *Apparatus:*

12.1.2.1 *Mixer*, planetary

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[11] ASTM General Purpose PVC Refere able from B. F. Goodrich Chemical Co., M Laboratory, P.O. Box 134, Avon Lake, OH

3.1.1 *Type GP*—General-purpose resins primarily intended for either dry blending, preblending, or thermoplastic processing.

3.2.1 *Type D*—Dispersion resins primarily intended for use in organosols and plastisols. As a class, these are small in particle size.

3.2 *Grades*—This specification provides for as many grades of resin as may be selected from the possible combinations of requirements in Tables 1 and 4. A grade is designated by first indicating the type (GP or D), followed by cell numbers for each property in the order in which they are listed in Tables 1 and 4. Where there is no interest in a property, a "0" is entered in place of a cell number. Should it be desirable, a cell limit may be extended by half the cell range into the next higher or lower cell, but not both. When this is done, it is indicated by a dash above the cell number ($\bar{n}$) if the extension is into the higher cell, or a dash below ($\underline{n}$) if into the lower cell. Extension of cell limits applies only to cells where ranges of properties are allowed and not where maximum or minimum values are specified. The cell number of the first property (dilute solution viscosity) is separated from those that follow by a dash.

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4. General Requirements

4.1 The resin shall be in powder form.

4.2 The resin shall conform to the requirements of Table 1 or 4 as specified by the type and grade designation agreed upon between the purchaser and the supplier.

NOTE 3—Properties not covered, such as heat stability, color, and volatile loss, may also be important for application performance in compounds.

5. Sampling

5.1 Unless otherwise agreed upon between the purchaser and the supplier, the material shall be sampled in accordance with the sampling procedure in Practice D 1898.

6. Number of Tests

6.1 One set of test specimens as prescribed in Sections 8 to 15 shall be considered sufficient for testing each batch.

7. Retest and Rejection

7.1 If any failure occurs, the materials may be retested to establish conformity in accordance with an agreement between the purchaser and the supplier.

8. Packaging and Marking

8.1 *Packaging*—The material shall be packaged in standard commercial containers, so constructed as to ensure acceptance by common or other carriers for safe transportation at the lowest rate to the point of delivery, unless otherwise specified in the contract or order.

8.2 *Marking*—Unless otherwise agreed upon between the purchaser and the supplier, shipping containers shall be marked with the name of the material, type and grade designation, quantity contained therein, and, as defined by the contract or order under which the shipment is made, the name of the supplier, and the number of the contract or order.

8.3 All packing, packaging, and marking provisions of Practice D 3892 shall apply to this specification.

TEST METHODS

9. Dilute Solution Viscosity

9.1 Method D 1243.

10. Apparent (Bulk) Density

10.1 Methods D 1895.

11. Sieve Analysis

11.1 Method D 1921.

NOTE 4—Method D 1705 may be substituted at the option of the purchaser and the supplier.

NOTE 5—Specifications for sieve analysis (Table 1) are primarily intended to control fines.

12. Brookfield Viscosity

12.1 Method D 1824. Take readings using a Brookfield RVF viscometer at 20 rpm with a No. 6 spindle. Prepare the plastisol sample as follows:

12.1.1 *Plasticizer*—Di (2-ethylhexyl) phthalate (DOP), Type I in Specification D 1249.

12.1.2 *Apparatus:*

12.1.2.1 *Mixer*, planetary-gear type,

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[11] ASTM General Purpose PVC Reference Standard is available from B. F. Goodrich Chemical Co., Manufacturing Services Laboratory, P.O. Box 134, Avon Lake, OH 44012.

equipped with flat beater mixing paddle.[12]

12.1.2.2 *Vacuum Desiccator*, capable of being evacuated to 133 Pa (1 mm Hg).

12.1.3 *Procedure:*

12.1.3.1 Condition the mixing bowl and materials to 23 ± 1°C. Weigh 500 ± 0.5 g of resin into the mixing bowl. Weigh 300 ± 0.5 g of plasticizer and add it directly on top of the resin in the mixing bowl. Hand mix with the flat beater for 1 min.

12.1.3.2 Mount the bowl on the mixer and mix for 5 min at the No. 1 speed. Stop the mixer and scrape down the sides of the bowl and the beater. Resume mixing at the No. 2 speed for an additional 15 min. Note and record the temperature of the plastisol immediately after mixing. The temperature rise must not exceed 5°C. Use a cooling bath if necessary.

12.1.3.3 Place the mixing bowl in the desiccator, evacuate to 133 Pa (1 mm Hg), and allow it to remain in the desiccator for an additional 10 min after the foam collapses. Consider the time in the desiccator as part of the normal aging period. Take care to ensure that the plastisol does not overflow the container during evacuation.

13. Severs Viscosity

13.1 Method D 1823. Determinations shall be made through a 3.18 ± 0.13-mm (0.125 ± 0.005-in.) diameter orifice at a gas pressure of 0.69 MPa(100 psi). The plastisol sample shall be prepared in accordance with 10.1.1 to 10.1.3.

14. Electrical Conductivity of Water Extract

14.1 *Summary of Method*—This test is intended to distinguish between electrical and nonelectrical grades of unprocessed resin. In general, the test will not detect relatively small differences among different lots of electrical grade resin. A water dispersion of the resin is boiled for a short time and the electrical conductivity of the solution is measured. The conductivity of the water extract results from ionic impurities in the resin [illegible] adversely affect its use for electrical insulation.[13] Electrical grade resins generally yield conductivity values less than 6 μS/cm · g.

14.2 *Definitions*—See 2.1 of Method D 1125.

14.3 *Apparatus:*

14.3.1 *A-C Wheatstone Bridge*, having a range up to 250 000 Ω, a 100 ± 50-Hz oscillator and a sensitive null point indicator with minimum accuracy of ± 2 %.

14.3.2 *Dip Cell*,[14] having platinum electrodes and a cell constant of about 0.1 cm^{-1}, similar to the one shown in Fig. 1. The cell shall be prepared and calibrated in accordance with Section 45 of Methods D 202.

14.3.3 *Thermometer*, equivalent to or better than ASTM Partial Immersion Thermometer, having a range from −20 to +150°C and conforming to the requirements for Thermometer 1C in accordance with Specifications E 1.

14.3.4 *Electric Hot Plate.*

14.4 *Reagents:*

14.4.1 *High-Purity Water*—Water having a conductivity not greater than 2.5 μS/cm, prepared in accordance with 46.1 of Methods D 202 or the equivalent.

NOTE 6—A high-purity water may also be obtained by passing ordinary distilled water through a dual-bed ion exchange column packed with an appropriate resin.[15]

14.4.2 *Isopropyl Alcohol*, ACS reagent grade.

14.5 *Procedure:*

14.5.1 Place a resin sample weighing 2.00 ± 0.01 g in a 250-mL Erlenmeyer flask that has previously been rinsed twice with boiling, high-purity water. Add 5.0 ± 0.5 mL of isopropyl alcohol to the sample, and swirl the mixture until the resin is uniformly wet. Add 100 ± 1 mL of boiling, high-purity water, set a watch glass on top of the flask, and boil gently for 5 min. Cool rapidly to 23 ± 1°C. Allow the resin to settle, then place the dip cell in the flask so that the electrodes are completely immersed, as shown in Fig. 2. Measure the resistance on the most sensitive scale of the bridge after 30-s immersion. Perform determinations in duplicate.

14.5.2 Between measurements, rinse the cell thoroughly in high purity water and gently shake off any water clinging to the surface.

14.5.3 *Blank*—Make duplicate parallel determinations using 5 mL of isopropyl alcohol and 100 ml of high-purity water.

14.5.4 *Calculation*—Calculate the electrical conductivity of the extract solution as follows:

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[12] A Hobart Model N-50, manufactured by the Hobart Manufacturing Co., Troy, OH, has been found satisfactory for this purpose.

[13] DeCoste, J. B., and Siratelli, B. A., "Characterization of PVC Resins by the Conductivity of Solvent Extract," *Rubber Age*, Vol 87, pp. 279–285.

[14] The cell illustrated is a Leeds and Northrup Conductivity Cell No. 4920. Other cells are available from Beckman Instruments, Inc., Cedar Grove, NJ 07009 and Rutherford Research Products Co., Rutherford, NJ 07070.

[15] Amberlite MB-1, obtainable from the Rohm and Haas Co., Philadelphia, PA, is satisfactory for this purpose.

$$\text{Electrical conductivity, } \mu\text{S/cm} \cdot \text{g} = [(L/R_2 - L/R_3)/m] \times 10^6$$

where:

L = cell constant,
R_2 = resistance, Ω of extract solution,
R_3 = resistance, Ω of blank, and
m = sample weight, g.

14.6 *Report*—Report the average of duplicate determinations of electrical conductivity in μS/cm · g of sample.

14.7 *Precision and Accuracy*—The precision of the method, calculated by analysis of the round-robin data from four laboratories, is as follows:

14.7.1 *Repeatability*—Coefficient of variation (average of replicates) within a laboratory of 14.7 %.

14.7.2 *Reproducibility*—Coefficient of variation (average of replicates) between laboratories of 17.2 %.

15. Plasticizer Sorption

15.1 *Scope*—This method covers the measurement of the amount of plasticizer that a resin can absorb at the standard laboratory temperature. Plasticizer sorption is one of the parameters for judging the dry blending properties of a resin. This method is similar in many respects to that employed in Method D 281.

15.2 *Apparatus:*

15.2.1 *Platform Scales or Balance*, 0.01-g accuracy.

15.2.2 *Glass or Glazed Porcelain Plate*, 254 by 254 by 6.4 mm (10 by 10 by 0.25 in.), minimum.

15.2.3 *Spatula*, with width and shape to fit mold cavity (see Fig. 3).

15.2.4 *Dropping Bottle*, 60-mL capacity.

15.2.5 *Mold*, aluminum or brass, as shown in Fig. 3.

15.3 *Plasticizer*—Di(2-ethylhexyl)-phthalate (DOP), Type I in Specification D 1249.

15.4 *Conditioning*—Determine plasticizer sorption at the Standard Laboratory Temperature of 23 ± 1°C.

15.5 *Procedure*—Weigh 5 ± 0.01 g of resin and transfer it to the plate. Obtain the gross weight, to the nearest 0.01 g of the dropping bottle about half full of DOP. Begin adding the DOP to the resin in 1-mL increments, using the spatula for mixing after each. When 4 mL have been added, change the rate to 2 drops at a time, making consistency determinations until the end point is reached. This is done by filling the mold, as it rests on the plate, with the mixture and then sliding the spatula under the charge. Lift the charge above the mold cavity with the spatula horizontal and then rotate the blade to a vertical position. The end point is reached when the mixture first slides off the blade. At this point, reweigh the dropping bottle and its contents. Make duplicate determinations.

Note 7—The mix portions used for consistency determinations should be returned to the main for each subsequent addition of plasticizer until the end point is reached.

15.6 *Calculation*—Calculate the plasticizer sorption as follows:

$$\text{Plasticizer sorption, parts of DOP per 100 parts of resin by weight} = (W_0 - W_1) \times$$

where:

W_0 = original weight of dropping bottle and DOP, and
W_1 = final weight of dropping bottle and DOP.

15.7 *Report*—Report the parts of DOP per 100 parts of resin by weight for the average of duplicate determinations.

15.8 *Precision and Accuracy*—The precision of the method, calculated by analysis of round-robin data from six laboratories, is as follows:

15.8.1 *Repeatability*—Coefficient of variation (average of replicates) within a laboratory of 2.1 %.

15.8.2 *Reproducibility*—Coefficient of variation (average of replicates) between laboratories of 5.0 %.

16. Dry Flow

16.1 *Summary of Method*—The dry flow characteristics of powdered resins bear a complex relationship to particle shape, structure, and size distribution. The flow may be measured by measuring the time for a prescribed volume of resin to flow through a standard funnel. The funnel orifice must be large enough to permit continuous flow of dry resins without bridging. The volatile content of the resin shall be within ± 50 % of the average specified by the manufacturer (see Method D 3030).

Note 8—Resins of abnormally high or abnormally low moisture content will exhibit reduced form flow. Extremely dry resins may develop static changes that will impede flow; damp resin will coalesce.

16.2 *Significance*—The dry flow of a resin as determined by this test is particularly significant in conjunction with plasticizer sorption for predicting the hopper feeding characteristics of dry blended resin-plasticizer compounds.

16.3 *Apparatus:*

16.3.1 *Metal Funnel and Cup*—See 8.1 and 8.2 in Methods D 1895.

16.3.2 *Stop Watch.*

16.4 *Procedure*—Put enough resin in the funnel so as to fill the cup to overflowing. Allow the resin to run into the cup. Level the resin in the cup. Close the small end of the funnel with the hand or a suitable flat strip of metal and pour the resin from the cup into the funnel. Quickly open the bottom of the funnel and start the stop watch at the same instant. Time the resin as it passes through the funnel. Repeat the procedure twice, using a different portion of resin for each determination.

16.5 *Report*—Report the average flow time in seconds for duplicate determinations.

16.6 *Precision and Accuracy*—The precision of the method, calculated by analysis of the round-robin data from seven laboratories is as follows:

16.6.1 *Repeatability*—Coefficient of variation (average of replicates) within a laboratory of 4.3 %.

16.6.2 *Reproducibility*—Coefficient of variation (average of replicates) between laboratories of 6.6 %.

QUALITY ASSURANCE PROVISIONS FOR GOVERNMENT/MILITARY PROCUREMENT

These requirements apply *only* to Federal/Military procurement, not domestic sales or transfers.

S1. Sampling for inspection and testing shall be carried out in accordance with the recommendations of Practice D 1898.

S2. Selection of Acceptable Quality Level (AQL) and of Inspection Level (IL) shall be made, with consideration of the specific use requirements. This is discussed in Sections 7 and 8 of the above document, with reference to Military Standard MIL-STD-105.

S3. In the absence of contrary requirements, the following values shall apply:

	IL	AQL
Defects of appearance and workmanship	II	2.5
Defects of preparation for delivery	S-2	2.5
Testing (products)	S-1	1.5
Testing (polymer, unfabricated)	S-1[A]	—

[A] Samples shall be drawn from the required number of units, and pooled for preparation of molded samples for mechanical properties evaluation.

TABLE 1 Type GP, General-Purpose Resin Requirements

Designation Order No.	Property	Cell Limits									
		0	1	2	3	4	5	6	7	8	9
1	Dilute solution (inherent) viscosity	unspecified	<0.70	0.70 to 0.79	0.80 to 0.89	0.90 to 0.99	1.00 to 1.09	1.10 to 1.19	1.20 to 1.29	1.30 to 1.39	≥1.40
2	Sieve analysis, percent through No. 200 (75-μm) sieve	unspecified	0 to 9	10 to 19	20 to 29	30 to 39	40 to 49	50 to 59	60 to 79	80 to 99	100
3	Apparent (bulk) density:										
	g/1000 cm³	unspecified	<144	144 to 232	233 to 328	329 to 425	426 to 520	521 to 616	617 to 712	713 to 808	≥809
	lb/ft³	unspecified	<9.00	9.00 to 14.50	14.51 to 20.50	20.51 to 26.50	26.51 to 32.50	32.51 to 38.50	38.51 to 44.50	44.51 to 50.50	≥50.51
4	Plasticizer sorption, parts DOP phr[A]	unspecified	<50	50 to 74	75 to 99	100 to 124	125 to 149	150 to 174	175 to 199	200 to 244	≥225
5	Dry flow, s/400 cm³	unspecified	. . .	. . .	<2.0	2.0 to 3.9	4.0 to 5.9	6.0 to 7.9	8.0 to 9.9	≥10	. . .
6	Conductivity, max, μS/cm · g	unspecified	. . .	. . .	<6	≥6	. . .	. . .	. . .	. . .	. . .

[A] phr = per 100 parts of resin.

TABLE 2 Requirements of Resin GP6-43054

Designation Order No.	Property	Unit	Requirement		Cell Code
			Min	Max	
1	Inherent viscosity		1.10	1.19	6
2	Sieve analysis	percent through No. 200 (75-μm) sieve	30	44 (39 + 10/2)	4
3	Apparent (bulk) density	g/1000 cm³ (lb/ft³)	233 (14.51)	328 (20.50)	3
4	Plasticizer sorption	parts DOP phr[A]	none		0
5	Dry flow	s/400 cm³	3.0 (4.0–2.0/2)	5.9	5
6	Conductivity	μS/cm · g	. . .	≥6	4

[A] phr = per 100 parts of resin.

TABLE 3 ASTM PVC Reference Standard No. 1 (General Purpose)

NOTE—The cell classification of this standard is GP5-15443.

	Method	Accepted Value[A]
Inherent viscosity	D 1243	1.018 ± 0.012
% through No. 200 Sieve	D 1921	1.3 ± 0.4
Apparent density, g/1000 cm³	D 1895	503 ± 5
Plasticizer sorption, phr	D 1755	101 ± 6
Dry flow, s/400 cm³	D 1755	2.6 ± 0.2
Conductivity, μS/cm · g	D 1755	1.0 ± 0.3
Porosity, cm³/g	D 2873	0.268 ± 0.022
Powder mix time, s	D 2396	163 ± 17

[A] Expected range for mean of 2 replicates (within a probability of 99.5 %).

TABLE 4 Type D, Dispersion Resin Requirements

Designation Order No.	Property	Cell Limits									
		0	1	2	3	4	5	6	7	8	9
1	Dilute solution (inherent) viscosity	unspecified	<0.90	0.90 to 0.99	1.00 to 1.09	1.10 to 1.19	1.20 to 1.29	1.30 to 1.39	1.40 to 1.49	1.50 to 159	≥1.60
2	Brookfield viscosity (RVF), poise	unspecified	0 to 24	25 to 49	50 to 74	75 to 99	100 to 124	125 to 149	150 to 174	175 to 199	>199
3	Severs viscosity, poise	unspecified	0 to 49	50 to 99	100 to 149	150 to 199	200 to 299	300 to 499	500 to 999	1000 to 1499	>1499

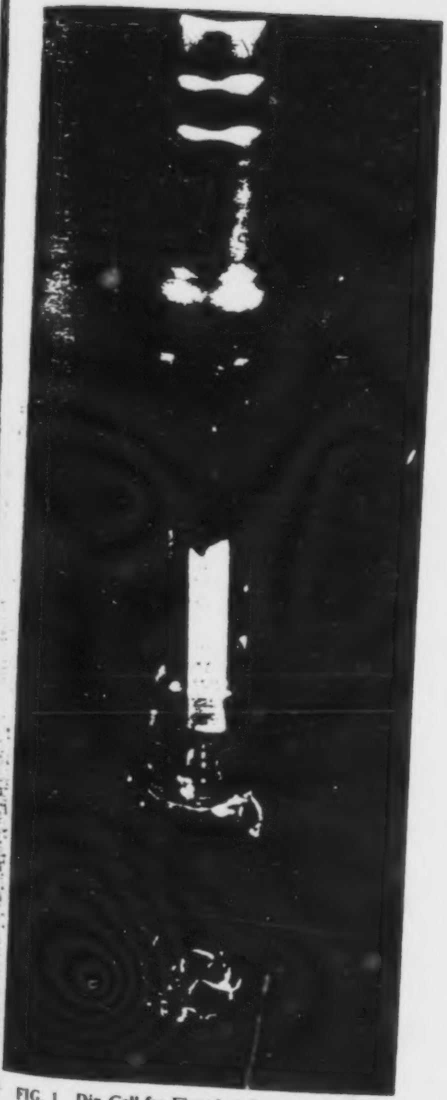


FIG. 1 Dip Cell for Electrical Conductivity Test.

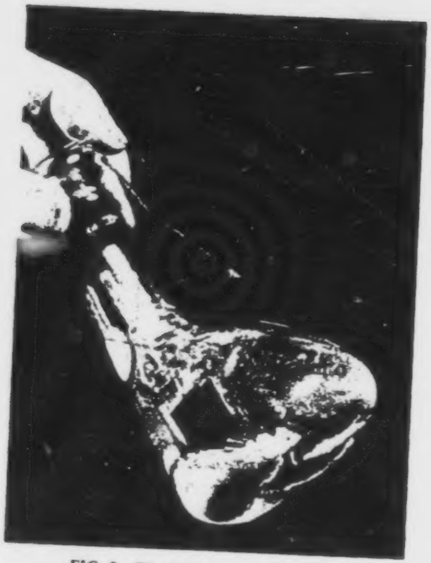
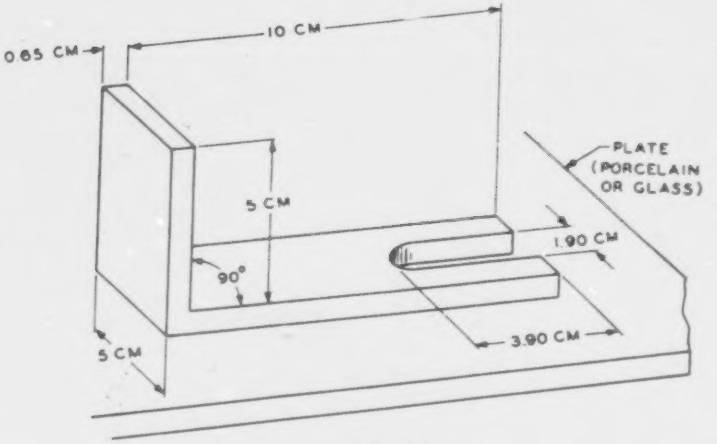


FIG. 2 Dip Cell Immersed in Flask.



TOLERANCE ON
ALL DIMENSIONS ±0.02 CM

FIG. 3 Mold for Plasticizer Sorption Test

The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, Pa. 19103.

Designatic

Standard
EPOXY

This standard is issued unde
year of original adoption or,
reapproval. A superscript ep

1. Scope

1.1 This specificatic
epoxy resins supplied a
can be used for casting
ting, adhesives, or rein
addition of hardeners i
causes these resins to p
products. The properti
be modified by the ad
reinforcements, extend
tropic agents, etc. The
also can be used as stab
agents; and they can b
reactive products.

1.2 It is not the funct
to provide engineering
purchaser in the selecti
specific end use. Ordinar
in Tables 1 and 2 are su
a material under this s
recommended that rout
ited to testing for such p

2. Applicable Documents

2.1 *ASTM Standards:*
D 445 Test Method fo
of Transparent and
the Calculation of D
D 1544 Test Method fo
Liquids (Gardner Co
D 1652 Test Method f
Epoxy Resins[4]
D 3892 Practice for I
Plastics[5]
2.2 *Military Standard:*
MIL-STD-105 Samplin
bles for Inspection b

3. Classification

3.1 The resins covered c

Oil absorption: Refining an ancient art

By T.H. Ferrigno, Improde, Trenton, N.J.

Oil absorption is a precise test—if it is used to determine packing fraction. Packing fraction helps to tell what to expect from a composite containing fillers, short-fiber reinforcements, and pigments alone or in combination—and how to solve some of the possible problems.

Oil absorption began as a putty maker's test to determine how much linseed oil was required with a suitable filler to obtain the correct working plasticity. The year was 1931 when ASTM D281, referred to as the rub-out test, was first accepted as a method. Putty makers have all but disappeared, but they have left us with an art far removed from its original purpose.

ASTM D281 still recites: "The test is *complete* when *exactly enough* oil has been incorporated with the pigment to produce a very stiff, *putty-like paste*, which does not *break* or separate." Note that there is no end point, but that the test is "complete."

It is not very difficult to see that "exactly enough" and "putty-like" are strictly judgments of the operator. Breaking, of course, refers to a lack of plasticity when the mass is worked with a spatula. In all, this test is supposed to measure a certain degree of plasticity without a test for plasticity—except in the judgment of the operator.

An award-winning paper[1] summarized all of the subjective problems of the ASTM test and concluded that only an instrumented mixer such as the Brabender Plastograph or Absorptometer (ASTM D2414) would provide "objective" data. Well, the differences between the rub-out and instrumented tests were so great in many cases that there is considerable doubt that either method is providing the necessary information.

What You Really Want to Know

Packing fraction (PF) describes the *maximum* fractional volume of filler, pigment, reinforcement or any nonmatrix particulate matter in a tightly packed mass wherein all of the particles are wetted and dispersed (separated) by the matrix and there is just enough matrix to fill the spaces between particles to produce a *continuous, void-free* system. This is then the point at which the composition is at maximum rigidity and infinite viscosity.

A well-established concept used to predict the properties of composites,[2] PF had its beginning in the paint industry, where it is called critical pigment-volume concentration, or CPVC.[3] Carefully collected oil-absorption data have served as a basis for numerous papers of which the referenced CPVC study[4] is typical. The rubber industry also uses a mechanized method employing the Absorptometer, to be described later, to characterize "structure," which is another term for PF.

If PF is considered to be the point of maximum rigidity (modulus) and infinite viscosity, it follows that its determination should provide a value for the maximum volume of particulate matter that can be obtained in a given system. The value obtained is then a combination of all of the properties of a given system.

Particle sizes, shapes, surface roughness, wetting characteristics, and all physical and chemical properties are then a function of the nature of the matrix and its physical and chemical properties, such as viscosity, surface tension, polarity and wetting. Indeed, PF is really a parameter since it is a value that depends on the conditions chosen.

Now, how is a "standard" method arrived at when all of the above variables have the potential to alter the data obtained? The following data will show that surrogate liquids representative of various polymers or matrices can be used as indicated in "Packing Fraction by Rubbing and Compaction," p. 22. But first, let us examine why the method of rubbing and compaction is superior to present instrumented methods.

Ah, There's the Rub!

With apologies to Mr. Shakespeare, our method is a considerable refinement of the so-called rub-out method of ASTM D281 and has been used to train operators to obtain the same data within the precision range of ±0.2 part by weight of oil per 100 parts by weight of particulate matter.

(continued)

The primary thing to keep in mind is that after all of the rubbing and working to ensure that the particles are uniformly wetted, the mass is then packed to *just* obtain a gloss on the pressed hemispherical cake, as illustrated in the figures. This indicates that all of the spaces between the particles, including those at the surface, are filled with liquid.

If this or any test is to be accurate, then it must ascertain the *maximum* volume of particulate material under the stated conditions, and this is where spatula and instrumented methods differ, as we shall see.

The Dollar Dilemma

Those of us who have had to justify every nickel (an inflated penny) of lab expense can readily appreciate the value of the cheapest and perhaps the most accurate way to evaluate packing properties. The equipment required costs about $90 for the balance, $2 for the spatula at the local gourmet shop, and about $1 for a 10-by-10-inch piece of scrap Formica laminated to plywood from a cabinet shop, for a total of $93. Any small weighing bottle such as an aspirin bottle and a supply of tubular swizzle sticks (ask a local bartender for a donation to science) complete the minimum equipment.

For those offended by physical exertion, the Absorptometer is currently available for about $6000 with a constant-rate burette, reservoir and tubing for cleaning. The Absorpticorder, also from C.W. Brabender, is considerably more expensive but a more versatile instrument. Both provide dynamic appraisals since resistance to mixing is measured as liquid is added to the powder. Some interpolation of the torque plot is necessary to establish the peak or maximum resistance that occurs somewhere near the PF, below which the resistance declines due to the lubricating effect of excess liquid.

Besides grinding particles between the rotor and wall, there is always a moving void in the mixture due to rotation of the mixing heads, and sustained compaction of the mass does not occur. Surface area of the bowl and mixing heads also introduces a significant difference, with finer, more absorptive materials resulting in much higher values than with the rubbing method.[8] The liquid-addition rate is standardized so that delayed sorption effects or true equilibrium wetting and packing are achieved only with very low-surface-area particles. Temperature control is preferable because of sample size and shear heating. Torque plots frequently reveal several peaks before the maximum, further indicating that equi-

Packing fraction by rubbing and compaction

Equipment

- Balance accurate to 0.01 percent or better
- Cappable bottles, 100 ml, or syringes
- Spatula, 4-inch blade of polished or stainless steel
- Board, nonsorptive, 10 by 10 inches or larger, of melamine/formaldehyde laminate with smooth finish bonded to 3/4-inch plywood
- Withdrawing tubes, 1/8-inch-diameter polyethylene or glass tubes
- Note: Although burettes may be used, cleaning for use with several liquids and inaccuracies due to density vs temperature make direct weighing preferred.

Materials

- Linseed oil, acid number 1 to 3 with 1 percent 2,6-ditertiary-butyl-para-cresol (BHT) antioxidant dissolved by warming

This provides a medium-polarity liquid that is stable for several months and provides consistent data. *Do not* use amine antioxidants since these will affect values obtained.

- Mineral oil, high-viscosity grade such as Drakeol 35 (Pennreco) for a low-polarity medium
- Other liquids representing the polarities or hydrogen bonding of polymers may be used.

Method

- For powders requiring up to 30 parts by weight of liquid to 100 parts by weight of powder, weigh 5.00 gm of powder and spread to about a 3-inch diameter on the board.
- Weigh the bottle containing the liquid with the withdrawing tube or the liquid-dispensing device in it.
- Distribute drops of the liquid on the powder to about 80 percent of the estimated requirement.
- Place the flat face of the spatula on the powder and smear with firm pressure. Scrape the board and fold the mass repeatedly until the smeared areas have a uniform color.
- Add liquid by drops until noticeable and uniform darkening occurs and the mass begins to adhere to the board (Figure 1).
- Lift the smeared material and layer it into a small pile, pressing firmly until adhesion to the board is noted. Scrape the board and compact the mass to form a hemispherical shape without cracks or loose powder. The mass may appear to

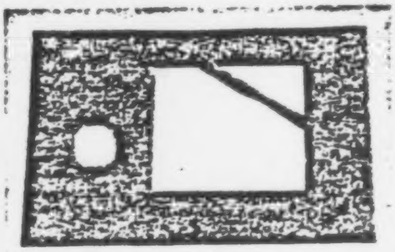


Figure 1. Left: 5.00 gm of filler. Right: filler on board at 0.50 gm of mineral oil, just beginning to adhere to board.

be dry at first, but additional pressing and smoothing will indicate whether it is becoming glossy.

- Cut and spread the cake and place drops or part drops of liquid on the spatula blade, smearing, folding and pressing as before. The end point is reached when the compacted cake adheres to the board and *just begins* to show a gloss (Figures 2 and 3). This indicates that all of the voids are filled including those between particles at the surface. Some very fine pigments or glassy fillers appear to be glossy well below the PF so it is advisable to use a 10X magnifier to see if the surface is truly wet or to apply a drop of liquid to the cake, which will absorb in several librium may not be established at the interpolated maximum torque.

All of the above describes a significant difference between the instrumental and rubbing method: the former is entirely *dynamic*, whereas the latter provides a *static* end point similar to the condition of a composite at rest. Since PF values for rubbing are generally higher, it follows that the method that yields higher values consistent with complete wetting and dispersion will more accurately describe PF.

Will the Composite Know the Difference?

PF gives the best seat in the house. When composite data are viewed from this vantage point, the message is clear. For example, Table I lists nonpolar mineral-oil and polar linseed-oil PFs by our method for several limestone fillers. The composite tells us that surface-modified[6] fillers yield lower viscosities and moduli with both polar (polyester) and nonpolar (polypropylene) matrices than the nonmodified fillers at the same volume concentrations.

PF data indicate the maximum filler volume obtainable in a continuous system, at which point it is a rigid mass. When fillers are used at practical concentrations, the relative filler volume (actual filler volume V_f divided by PF) indicates which is closer to the point of maximum rigidity. It may be seen that extremely low PF values for nonmodified fillers with nonpolar mineral oil will certainly produce much higher composite viscosities and moduli. Estimates of these values can be calculated by using equations from the handbook.[7]

PF differences are caused by the way particles pack together, and this is more important than any other physical property of fillers. Pigments and reinforcements are governed by more complex factors, but the same criterion applies when they are used in combination since PF is a summation of their collective size-distribution, shape and surface properties.

As filler usage becomes more refined, especially by way of using surface-modified types, it may be seen that fine and moderately fine (Supermite vs Vicron 15-15 or Camel-Wite) types may be improved to near equality. Their packing fractions provide a fundamental basis for comparison. Not to do so would give the false impression that finer fillers always have poorer packing properties.

Table II lists PFs of various fillers by our method to illustrate differences and similarities. Comparing precipitated calcium carbonate with the ground limestone fillers of Table I illustrates

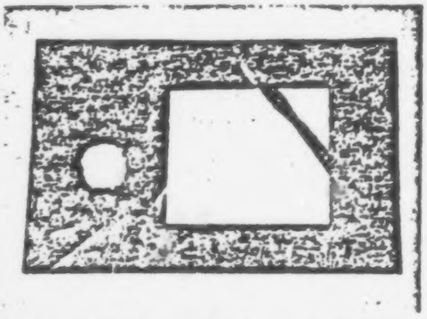


Figure 2. Right: end point at 0.52 gm of mineral oil. Note surface of pressed mass just beginning to show a gloss.

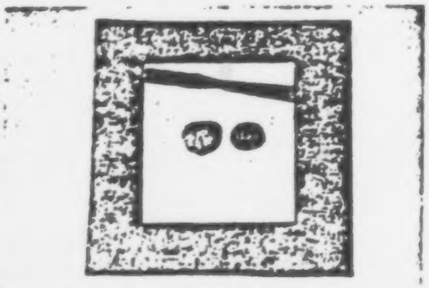


Figure 3. Left: 5.00 gm of processed mineral fiber at end point of 1.89 gm of linseed oil. Right: 5.00 gm of processed mineral fiber plus 2.0 gm of Atomite at end point of 1.82 gm of linseed oil. Note size and color of the pressed cakes.

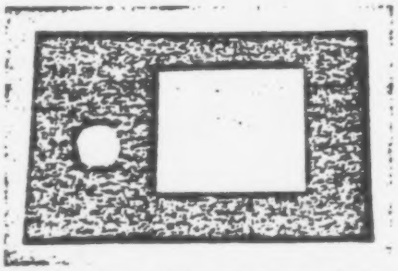


Figure 4. Right: filler at 0.54 gm of mineral oil. Note very shiny surface on pressed cake beyond end point.

minutes if the end point was not reached. Figure 4 shows a condition beyond the end point for comparison.

Calculate packing fraction (PF)
Weight of powder used/density = volume powder
Weight of liquid used/density + powder volume = total volume
Powder volume/total volume = PF, to 0.00X.

Notes

Precision is ± 0.01 gm, which calculates to total PF ranges of 0.007 to 0.003 for 1.5 to 0.5 gm/5.00 gm of limestone filler. This is well within the range of reliability for prediction of PF effects.

Accuracy depends on obtaining minimum values, which are established by replication and require that at least 20 minutes be spent in rubbing and packing. Finer powders require more working to overcome agglomeration, and up to 1 hour may be required to obtain reproducible results.

Linseed oil with 1 percent BHT will vary from 0.9291 to 0.9321 gm/cu cm at 20C (68F). Using 0.93 produces an error in accuracy of −0.1 to +0.2 percent or well within the bounds of precision. Temperatures exceeding 75F will introduce significant error.

If there is some question about the free-water content of the powder, that which is removed at 100C, determine packing fraction before and after drying and cooling in a desiccator. For low-surface-area fillers, free water does not alter PF unless it exceeds about 0.3 percent with moderate- to low-polarity liquids.

Once the board has been used, rub and wipe it, as well as the spatula, with paper towels to remove excess residual film. Do not wash or clean with solvents since the board surface will acquire a sorbed film that will provide more accurate and reproducible data.

Table I. Packing fractions of ground limestone fillers

Filler	Surface modified[1]	Average particle size,[2] microns	Surface area,[3] sq m/gm	Density, gm/cu cm	Absorption test, lb/100 lb filler			Packing fraction	
					Mineral oil[4]		Linseed oil[5]	Mineral oil	Linseed oil
Supermite (Thompson-Weinman)	No	1.0	7.2	2.71	26.0	1.76	14.8	0.0554	0.699
Supercoat (Thompson-Weinman)	Yes	1.0		2.61	15.8	1.20	13.2	0.680	0.730
Supermite[6] (Thompson-Weinman)	Yes	1.0		2.61	10.2	0.94	10.8	0.767	0.767
Vicron 15-15 (Pfizer)	No	3.0	3.5	2.71	22.2	1.68	13.2	0.593	0.722
Hi-Pflex 100 (Pfizer)	Yes	3.0		2.61	12.6	1.03	12.2	0.723	0.741
Vicron 15-15[6] (Pfizer)	Yes	3.0		2.67	10.4	0.91	11.4	0.759	0.757
Camel-Wite (Genstar)	No	3.4	3.0	2.71	28.8	2.12	13.6	0.529	0.716
Camel-Wite[6] (Genstar)	Yes	3.4		2.66	10.0	0.94	10.6	0.767	0.767
− 20 mesh	No	44.0	0.5	2.71	11.6	1.26	9.2	0.736	0.789
− 20 mesh[6]	Yes	44.0		2.70	7.5	0.89	8.4	0.812	0.804

[1] Surface modified; for example, Supercoat has 2 percent stearic acid and Hi-Pflex has a proprietary agent.
[2] Particle size from producers' literature.
[3] Surface area from producers' literature; calculated for − 20 mesh filler.
[4] Drakeol 35 (Penreco), density 0.876 at 20C (68F).
[5] Alkali refined with 1 percent BHT (see method), density 0.93.
[6] Experimental surface-modifying agents, patent applied for; all four are different.

↑ relative
absorption number

at calcium carbonate is extremely rptive when very fine. Although talc may have more than three times the rface area of the Camel-Wite, for exmple, it may have a similar mineral-oil absorption. This significant difference in surface properties is a factor in e use of these materials as polypropylene fillers. Again, low-surface-area wollastonite does not yield the high PF alumina trihydrate having four mes the surface area.

Short-fiber reinforcement, illustrated by processed mineral fiber, was tested by pressing and lightly rubbing without smearing to prevent degradaon of the brittle fibers. The mass was ightly spongy at the end point, but no iber degradation occurred. The combinaticn of 71 wt-% processed mineral ber with 29 wt-% Atomite produced a ignificant increase in PF. It must be kept in mind that these data may not be precise indicators of performance because the bulkiness of fibers would be reduced under the pressure of molding such a composite. Also, true random fiber orientation as obtained in the test probably is never obtained in a molded item. Nonetheless, these data should be related to processing and molded-product properties.

An Added Dimension

Although it would seem that the simplicity of the PF test implies some oversimplification, it is certainly better to use a direct means to establish a basic property than to use the empirical method of compounding, fabricating and testing when such laborious effort may not reveal differences that would have been evident based on PF.

Plasticizer "absorption" has been examined as a way to classify different fillers.[8] These data simply relate PF to various plasticizers having slightly different wetting and polarity properties, and imply that *only* the plasticizer is effective in determining "absorption."

It is doubtful that such data provide useful measures of how a filler influences physical properties since it is used in combination with plasticizers, stabilizers, other additives *and* polymer, all of which is fused to become the matrix. It would be more realistic to use a combination of plasticizer, additives and stabilizers, in the correct proportions, as the liquid in the PF test since all of these agents affect the wetting and dispersion properties of the filler.

Where plastisols are concerned, the particles of filler *and* dispersion resin form the discontinuous medium, and the plasticizer plus additives can be

Table II. Packing fractions of various fillers

Filler	Average particle size,[1] microns	Surface area,[2] sq m/gm	Density,[3] gm/cu cm	Packing fraction	
				Mineral oil[4]	Linseed oil[4]
Precipitated calcium carbonate	0.6	8.0	2.71	0.298	
Wollastonite P-4	5.5	1.5	2.9		0.646
− 325 mesh talc	4.4	10.0	2.74	0.538	
Alumina trihydrate	7.5	6.0	2.42		0.730
Processed mineral fiber	3.5[5]	<1.0	2.7		0.477
Processed mineral fiber, 71 wt-%	3.5[5]	<1.0	2.7		0.567
Atomite, 29 wt-%	3.0	2.8	2.71		0.567

[1] Particle size from producers' literature.
[2] From producers' literature or calculated.
[3] From producers' literature.
[4] Drakeol 35 (Penreco), density 0.876 at 20C (68F).
[5] Average fiber diameter.

used to determine PF. Such data will relate to viscosity in the liquid state but are not usable for predicting moduli and other physical properties because the resin becomes part of the matrix on fusion.

PF data add another dimension to processing also. At processing temperatures, thermoplastics expand 2 to 10 vol-%, whereas inorganic materials expand about one-tenth as much. The net gain in matrix volume is frequently adequate to provide better flow properties than would be calculated on the basis of room-temperature PF. Conversely, thermosetting resins may shrink about 1 to 5 vol-% on polymerization. Calculation of modulus of the fabricated composite therefore has to be adjusted for the density of the cured polymer.

Modulus is always increased when fillers or reinforcements are added to polymers. However, there are composites that may have moduli reduced when a fine pigment or filler is added. This occurs when the PF is increased by the more efficient packing of the particles. The reverse occurs if the PF is reduced, and these effects are more pronounced at high filler volumes and vice versa.

Subtle differences of this nature are often more noticeable on viscosity and impact resistance, which are decreased and increased, respectively, when low concentrations of titanium dioxide pigment, for example, are added.

The PF test adds a primary tool to composite formulating since such effects can be anticipated by examining additions of fine pigments or fillers that extend the particle-size distribution and result in more efficient packing.

The many ways PF influences composite properties have only been touched on. PF should be used as a fundamental basis for comparing various composites or the effects of fillers or reinforcements.

Conclusion

PF provides a fundamental basis for classifying fillers, reinforcements and pigments, alone or in combination in various composites. The test procedure given is reliable for determining PF and amenable to modification to suit specific conditions. PF adds a new and basic dimension to our understanding of composites and should become a basis for refinement and improvement of composite technology. ■

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A SYSTEM FOR DETERMINING THE OPTIMUM GRINDING COMPOSITION OF PAINTS IN BALL AND PEBBLE MILLS

By

FREDERICK K. DANIEL, *Consulting Chemist*

I. *Introduction*

The function of ball and pebble mills in paint manufacture is the uniform distribution of the pigments in the vehicle.

Usually the pigments are put in the mill with only a portion of the vehicle called for bv the formula, the balance being added subsequently in a separate operation. Therefore, a choice must be made how much of each vehicle component, that is binder and solvent, and how much vehicle, in all, should be added to the pigment for the grinding operation.

Of all the pigment-binder-solvent combinations there must be one which produces more finished paint of a given quality per unit of time than any other combination. This must be true of any paint and of any piece of milling equipment.

This optimum composition for each formula can be found by trial and error methods. An excellent study of the effect of composition and temperature on the output and quality of a single formula in a pebble mill was published recently by Baker and Vozzella.[1] It is the aim of every paint production man to know the optimum mill composition of all his formulae without going through such an extensive study and, moreover, to be able to take into account variations in the properties of his raw materials.

It is our thesis that this goal can be approached closely in a great number of paint systems by the application of a simple technique which yields pertinent production data from laboratory experiments.

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This thesis was tested extensively for three years in several large paint plants. The resultant improvements in the quantity and quality of paint output led to the adoption of the new technique in every instance.

It is now presented to the paint industry for critical review and possible improvements in the hope that it will become a generally useful tool in paint production.

The method is based on two premises:

1. That there are, today, only a few coarse pigments and inerts which must be broken down in the milling operation into smaller particles. The particle size of the vast majority of pigments used in paint production is so small that it needs no further breakdown for even the finest enamels. The function of milling is to pull apart, to disperse and to wet agglomerations (flocculates) of these primary particles. In the loose terminology of the paint industry (which will be followed here), "grinding" usually means wetting and dispersing of flocculates.

Relatively weak forces are sufficient to accomplish this type of "grinding", while the breakdown of primary particles and hard aggregates requires much greater forces.

2. That closed mills (ball and pebble mills) are dual function machines which operate

(a) by impact, resulting from the collision of the grinding elements (balls and pebbles), and

(b) by inter-particle shear, resulting from the paste motion caused indirectly by the moving grinding elements.

In the minds of most paint men closed mills are associated with the strong impact forces and the size reduction of the hardest pigments. Under certain conditions, however, the shear component, although a much weaker force, can be made to contribute many times as much "grinding" work as the impact. If so used, ball and pebble mills will turn out much more paint, and of a higher quality, than if used primarily as impact tool.

It can be shown that the shearing action in the mill becomes the dominant dispersing force when the pigment and inert concentration is high and at the same time the viscosity of the grinding vehicle is low.

When both of these conditions are fulfilled, the flocculates and particles rub against each other most effectively and most frequently and thus cause wetting and dispersion (de-flocculation) in the shortest possible time. The limiting factor on pigment concentration is the consistency of the mass. It must not be so high that the motion of the grinding elements is unduly impeded or stopped altogether.

The questions raised by this statement are:

(1) What is the highest possible pigment concentration obtainable for a given consistency? How can it be determined?

(2) What is the proper grinding consistency?

The methods described below seem to give sufficiently accurate answers and to be simple enough to serve as a basis for a more scientific determination of grind composition than the present rule-of-thumb approach to this problem.

II. *The Determination of the Maximum Pigment Concentration*

A. *Rheology of Pigment Suspensions:*

It has been shown in a previous paper[2] that the amount of liquid required to just barely wet a given amount of powder varies slightly with the nature of the liquid, but that the amount of liquid needed to make this paste flow varies greatly. The factor which controls the flow of the powder-liquid system is primarily the state of flocculation or deflocculation of the particles in suspension. In a deflocculated (dispersed) system each particle is independent of all the other particles present, and in this state the amount of liquid required to make the mixture flow is only slightly higher than that required to just wet the powder. A few percent additional liquid will transform a stiff, almost dry and unworkable paste into a free-flowing mass. Hence, the powder concentration of the free-flowing mass differs only slightly from the concentration of the semi-rigid mass. The margin for error as to what constitutes the highest possible pigment concentration for milling is very small in this case. (Fig. 1a) Not so with flocculated systems. (Fig. 1b) The transformation from the just wetted, highly plastic state to the quasi-liquid of low yield value is so gradual and spread out over such a concentration range that it is hard to decide which is the highest pigment concentration at which the material can move in the mill. The pigment concentration of a flocculated system at flow consistency may be only one-half to one-third as high as in a corresponding deflocculated system.

There are many intermediate stages between complete deflocculation and flocculation. Fortunately, many paints, and especially enamels, belong to the deflocculated group, and therefore display a sharply definable, high pigment concentration at the transition point from fluid to semi-rigid state. The

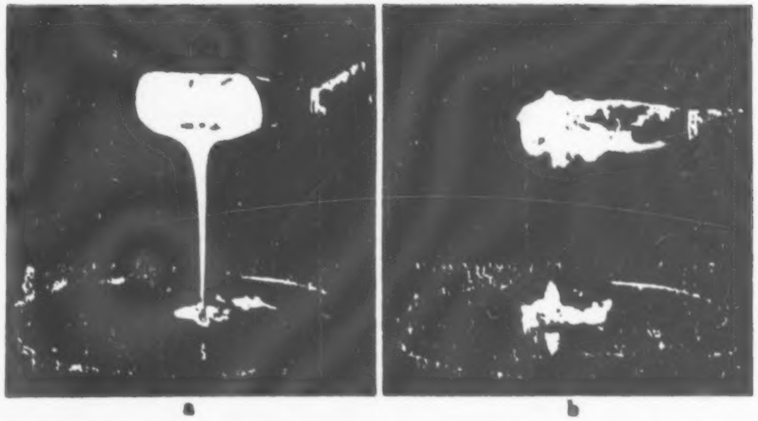

Figure 1. a. Deflocculated paste (40% pigment A, by volume) showing characteristic flow at high pigment concentration.
b. Flocculated paste (15% pigment A, by volume) showing characteristic plastic state even at low pigment concentration.

degree of flocculation or deflocculation is a specific characteristic of each suspension and depends on the nature of the components present. Sometimes small quantities of moisture will change the characteristics. Pigment "A" may be deflocculated in vehicle "X" and flocculated in vehicle "Y", and with pigment "B" the situation may be the other way around. One lot of pigment "A" may disperse better than another. For hydrophobic pigments an aromatic solvent may be a poorer dispersing medium than an aliphatic one, in spite of its higher solvency for the binder.

This high degree of specificity makes all generalizations in the paint field so difficult. However, a few regularities can be observed:

(1) Of two liquids with equal dispersing power for a pigment "A", the one of lower viscosity will permit higher pigment concentration for a given viscosity or shearing stress.

(2) Of two liquids with equal dispersing power and equal viscosity, the one with higher solvent content will usually permit the higher pigment concentration for a given consistency.

It follows that pure solvents, being low in viscosity and completely volatile should permit the highest pigmentation. However, the common solvents have no deflocculating power for any of the common pigments and inerts and therefore they cannot be used as the sole vehicle in the mill. Pigments milled in solvent are quickly wetted but remain flocculated. They cannot be uniformly distributed in the balance of the paint ingredients and

give dull finishes with brush-marks, indicating that dispersio is really the most important function of a paint mill.

While solvents are unsuitable as grinding vehicles because o their lack of dispersing power, the vehicles with dispersin power such as oils, varnishes and resins are usually quite viscou and for this reason, and because of their high solid content, limi the pigment concentration at the prescribed consistency. Mix tures of fixed vehicle and solvent permit higher pigment con centration than either component alone. The problem is merel how to determine the proportion of each of these component and then to determine the maximum percentage of pigmen which can be incorporated in the vehicle mixture.

Theoretically the answer is simple and unequivocal: Regar the fixed vehicle merely as a dispersing agent for the powder suspended in solvent and use the least amount, i.e., just enoug to disperse the last of the flocculates present in the system At this point the lowest viscosity and solid content of the vehicl consistent with the necessary dispersing characteristics, i reached, and therefore maximum pigment concentration i obtained.

As a practical solution to the problem the following exper mental procedure was adopted.

B. *Description of Laboratory Technique:*

To ascertain the highest pigment concentration for a give pigment-solvent-binder combination a certain amount of pi ment, e.g. 20 gms, is placed in a 100 ml beaker and a solutio of, say, 30% binder solids and 70% solvent is added under co tinuous kneading and rubbing with a fire polished glass r until a heavy, smooth paste is obtained. More solution is th gradually added until the mass can be stirred without mu resistance. Then the glass rod is quickly lifted out of the beak and the material clinging to the vertically held rod is permitt to run off. A distinctly recognizable and reproducible state fluidity exists which is referred to as the Flow Point. The Flo Point (F. P.) is said to be reached when only a thin, even fil of material remains on the rod, and when the last few dro falling in one to two second intervals, appear to break off t tip of the rod with an elastic snap-back like a piece of rubb breaking under load. The amount of solution needed to rea this F. P. is recorded either in terms of volume or weight solution. This test is repeated with solutions of different bind content, from 5% up to 40% maximum and the F. P.s a plotted: the amount of solution on the ordinate and the concentration of the solution on the abscissa. The resulting curve, Fig. 2a, usually goes through a minimum and at this point the maximum pigment concentration of the particular binder-solvent-pigment system is reached. The pigment concentration at this point is calculated as follows:

EXAMPLE: With 20 grams of Red Oxide the lowest F. P. value is obtained at 8.1 grams solution of 20% concentration.

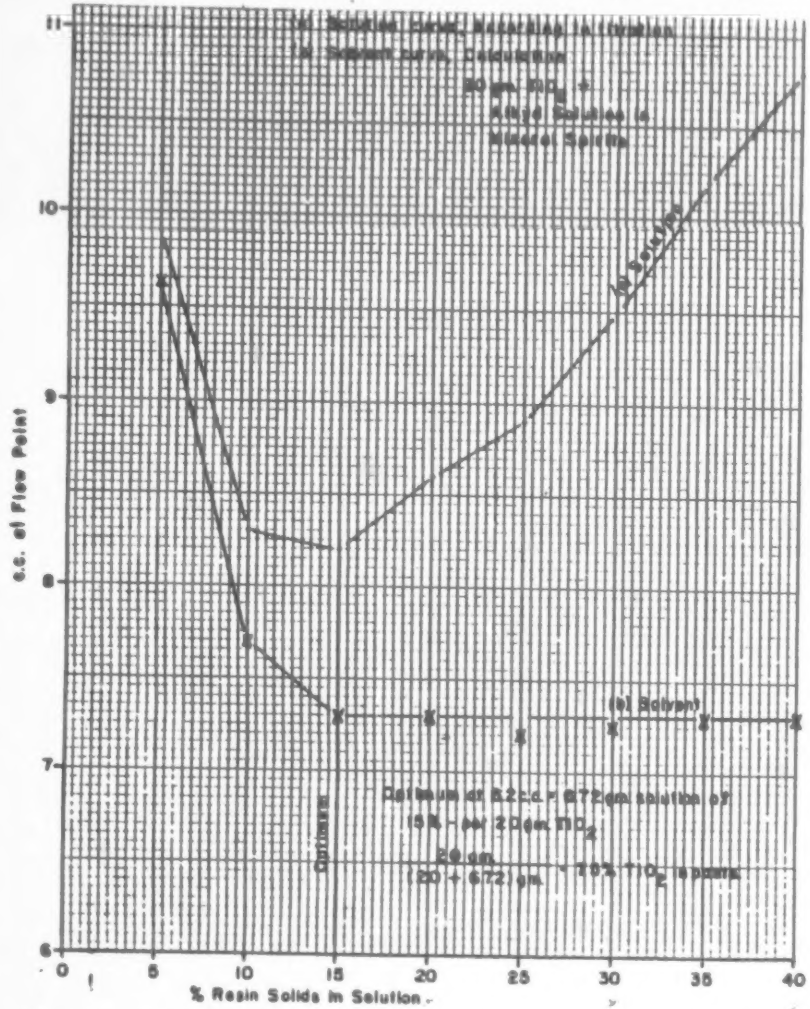

Figure 2. Determination of Optimum Grind Composition by Flow Point Method.

1 lb. Red Oxide, therefore, requires $\frac{454}{20} \times 8.1 = 184$ grams solution. If the original varnish comes in the form of a 50% solution, $\frac{20}{50} \times 184 = 73.6$ grams of varnish and 110.4 grams solvent are required to bring 1 lb. of this particular Iron Oxide to its F. P. consistency. This represents a pigment concentration at the optimum point of $\frac{454}{454 + 184} \times 100 = 71\%$.

A brief comment on the F. P. curve and an explanation of the minimum so frequently encountered seems in order at this point: As the first few percent of fixed vehicle are added to the pure solvent, the amount of solution required for reaching F. P. consistency is sharply reduced, because the system is no longer completely flocculated. As flocculation decreases with increasing fixed vehicle concentration, less and less solution is needed to reach the Flow Point. When all the pigment is deflocculated, the curve reaches its minimum and the pigment concentration its maximum. As solutions of even higher fixed vehicle content are used, the curve rises again. This rise is due to the diminishing proportion of solvent in the solutions of increasing concentration. It is revealing to compute the amount of solvent contained in each of the solutions used for Flow Point determinations and then plot the solvent vs. concentration curve. This has been done in Fig. 2b. It will be noted that the curve levels out horizontally as is to be expected, once full deflocculation is obtained. This means that an excess of binder contributes nothing to the flow, if it is a solid, and little, if it happens to be a liquid. The presence of more fixed vehicle than what is needed for its dispersing function merely lowers the maximum pigment concentration of the system and increases the grinding time due to increased vehicle viscosity.

For good dispersions the reproducibility of the results is surprisingly good. The same operator can duplicate his results within two or three percent after a few days' practice. The variation in results between two operators is insignificant, once they have agreed on what constitutes the F. P. For poor dispersion the variation in results is greater.

It is possible to determine the F. P. by instrument, but this procedure, while more accurate, is very much slower than the beaker test. It is therefore not recommended for use by individual paint plants.

III. *Relationship Between Laboratory Results and Mill Performance*

The question arises: How is the Flow Point of the beaker test related to the flow under actual conditions in the mill? It has been found that for soft pigments and inerts the rubbing and stirring action of the glass rod does a surprisingly good wetting and dispersing job. A fineness of 3-4 on the North Standard can readily be obtained. Hence the Flow Point values in the beaker are, for practical purposes, the same as those obtained after running the mix in a pebble mill for several hours. This does not hold, of course, for hard pigments or for pigments which wet very poorly. Pigments belonging to this group show a F. P., but this is the F. P. of the agglomerates, not that of the primary particles. The gritty appearance on the wall of the beaker and on the glass rod betrays this false F. P. of the agglomerates at once.

It is necessary in the case of these pigments to grind them with a vehicle of about 25% binder content in a ball mill for several hours, and then determine once more the Flow Point with an aliquot portion of the ground paste. This corrected Flow Point has been found to be closely related to the maximum grinding efficiency for the particular pigment.

The refined method of Flow Point determinations is needed for a small group of pigments only, such as carbon black beads, carbon blacks of very fine particle size, several hard organic colors and a few inorganic ones. The Flow Point of the vast majority of pigments can be determined satisfactorily by the simple beaker method.

What effect has the temperature difference between beaker test and mill paste on the consistency correlation of plant and laboratory? In large mills temperatures of 25-40° C. develop during grinding, and 40-60° C. in ball mills are common.

When the grinding vehicle is of high viscosity, the temperature effect is a very significant factor for the consistency. In such cases one often finds that for many hours hardly any grinding takes place; only a mixing. As the heat of the mixing operation in the mill increases, the viscosity of the vehicle drops sharply and grinding begins. This no-grinding period can be shortened materially by shutting off the cooling water and even more by letting steam into the jacket of the mill. This has been done in some plants to good advantage and the procedure may be recommended where the formulation does not allow much solvent to be added to the material, and provided fixed vehicle does not heat-polymerize too readily. However, for pastes with a low viscosity vehicle it is unnecessary and even undesirable to work at elevated temperatures. In such systems the viscosity change accompanying the temperature change is small. For this reason temperature corrections for grind compositions derived by F. P. determinations are generally unnecessary.

It appears from the above discussion that the Flow Point determined by the beaker test is closely related to the maximum pigment concentration in the mill for the majority of the pigments used in paint manufacture today.

IV. *Application*

A. *Example of Complete Technique:*

The complete technique for determining the optimum grind composition may be illustrated by the case history of an olive drab enamel of the following composition:

EXAMPLE 1:

110	lbs	Chrome Yellow
144	lbs	Calcium Carbonate
36	lbs	Prec. Red Oxide
34	lbs	Lamp Black
6	lbs	Paste Drier
2	lbs	Aluminum Stearate
100	gls	Medium Oil Alkyd (50% solids)
28	gls	Long Oil Alkyd (70% solids)
60	gls	Mineral Spirits
2.5	gls	Drier

Step 1:—F. P. Determination:

Five mixtures of the medium oil alkyd (50%) with varnolene are prepared and placed into burettes—

Mixture 1 30cc alkyd + 20cc mineral spirits
" 2 25cc " + 25cc " "
" 3 20cc " + 30cc " "
" 4 15cc " + 35cc " "
" 5 10cc " + 40cc " "

Each of the four pigments are titrated, in turn, to the F. P. with each of these solutions. The result is listed below.

Mixture	Chrome Yellow	Calc. Carb.	Red-Oxide	Lamp Black
	20 gms	10 gms	20 gms	10 gms
1	10.3cc	10.4cc	10.8cc	24.6cc
2	10.1cc	9.4cc	10.2cc	23.4cc
3	9.4cc	8.8cc	9.9cc	22.2cc
4	9.0cc	8.9cc	9.9cc	21.0cc
5	9.9cc	9.2cc	10.5cc	22.7cc

From these figures it is concluded that Chrome Yellow and Lamp Black have their optimum near the 15:35 alkyd to solvent ratio, while the Red Oxide and Calcium Carbonate require about a 20:30 ratio. Accurate determinations can be made by plotting the full F. P. curves as described earlier.

The vehicle and solvent requirements per pound of each pigment are calculated from these data as follows:

Per 1 lb.	Total Solution in cc	Vehicle in gal.	Solvent in gal.
Chrome Yellow	$9.0 \times \frac{454}{20} = 204$	$\frac{15}{50} \times \frac{204}{3785} = .0162$	$\frac{35}{50} \times \frac{204}{3785} = .0377$
Cal. Carbonate	$8.8 \times \frac{454}{10} = 400$	$\frac{20}{50} \times \frac{400}{3785} = .0423$	$\frac{30}{50} \times \frac{400}{3785} = .0635$
Prec. Red Oxide	$9.9 \times \frac{454}{20} = 225$	$\frac{20}{50} \times \frac{225}{3785} = .0238$	$\frac{30}{50} \times \frac{225}{3785} = .0356$
Lamp Black	$21.0 \times \frac{454}{10} = 952$	$\frac{15}{50} \times \frac{952}{3785} = .0755$	$\frac{35}{50} \times \frac{952}{3785} = .176$

Step 2:—Computation of the Amount of Vehicle and Solvent: This is done by multiplying the above vehicle and solvent requirements per 1 lb. with the number of pounds of pigments called for by the formula, in this case—

	Vehicle in gal.	Solvent in gal.
110 lbs Chrome Yellow –	110 × .0162 = 1.78	110 × .0377 = 4.14
144 lbs Calc. Carbonate	144 × .0423 = 6.08	144 × .0635 = 9.13
36 lbs Red Oxide	36 × .0238 = 0.86	36 × .0356 = 1.28
34 lbs Lamp Black	34 × .0755 = 2.56	34 × .176 = 5.98
Total	11.28 gal.	20.53 gal.

Step 3:—Grind Composition and Mill Charge:

The comparison of a conventional ball mill composition for this formula and the "concentrate grind" computed above is as follows:

	Conventional	Concentrate Grind
Chrome Yellow	110 lbs.	110 lbs.
Calcium Carbonate	144 "	144 "
Red Oxide	36 "	36 "
Lamp Black	34 "	34 "
Paste Drier	6 "	6 "

	Conventional	Concentrat Grind
Aluminum Stearate	2 "	2 "
Medium Oil Alkyd (50%)	66 gal.	11.3 gal.
Varnolene	10 "	20.5 "
24% Lead Naphthenate	1 "	1.0 "
Total Grind	90 gal.	45.8 gal.

In the "Concentrate Grind" only one-half the paste volum has to be ground as in the conventional composition. Sinc 90 gls is the correct mill charge, the new formula can be nearl doubled, that is to say, twice as much finished enamel is produced in a single mill operation. Grinding time, in this instance is cut from thirty hours to twenty hours for a product of equa fineness. If the concentrate grind is milled for thirty hours, finer, glossier enamel with less floating is produced than the conventional grind produces at any milling time.

In this case then the output of finished paint per hour is jus tripled, and this increase is not exceptional. At first glance i may seem as if the determination of grind composition is quit an involved and time-consuming process. Actually, howeve the application becomes progressively simpler as a backlog o F. P. data is accumulated. The assembled data are best tabulate as shown in the Sample Sheet below:—

SAMPLE SHEET

Flow Point Data

FIXED VEHICLE: *Varnish "A" (50%)*
Solvent: *Varnolene*

Per 1 lb. pigment	Solution cc	Vehicle gal.	Solvent gal.	Concentration (or dilution
Chrome Yellow	204	.0162	.0377	15:35
Calcium Carbonate	400	.0423	.0635	20:30
Lamp Black	952	.0755	.176	15:35
Red Oxide	225	.0238	.0356	20:30
....				
....				
....				
.... Etc., etc.				

Plants which use the weight system throughout can, of course, adapt this form to suit their purpose.

The F. P. determinations are carried out separately for each pigment and computed on a one pound basis, because in this way the data are available for all formulations in which this pigment-vehicle-solvent combination occurs. If it weren't for this, it would be simpler to mix together in proper proportion all the pigments of a given formula and determine their combined F. P. in one titration.

By collecting the individual F. P. data, the determination of optimum grind composition can be reduced largely to a matter of computation. Raw material suppliers can assist the paint manufacturer by establishing the F. P. data for their respective products in combination with widely used vehicles or pigments.

B. *Shortcuts and Modifications:*

Numerous F. P. determinations show that most pigments have their optimum at about 20% vehicle solids. Only a few pigments of very fine particle size need more vehicle solids for complete dispersion, and a few others need less vehicle solids, usually around 13-16%. Often these highs and lows cancel each other out in formulations involving several pigments. It is therefore possible to reduce the number of F. P. determinations from the full five or six concentrations for a complete F. P. curve, to one or two concentrations, without sacrificing much of the advantages of the method. This shortcut appeals to the practical paint production man who does not have much laboratory help for this kind of work. He will start out with a solution of 20% vehicle solids (by weight) and 80% solvents, and take additional points on the F. P. curve only if he finds himself short of solvents in his formula or if he gets a pigment seeding-out upon addition of the balance of vehicle to the ground paste. This seeding-out is indicative of insufficient dispersing agent.

Generally, the deviation from the optimum formulation by the single F. P. determination amounts to no more than a few percent in terms of paint output and grinding time. A greater deviation from the optimum is sometimes enforced by lack of solvents present in the formula. Highly pigmented paints, especially, do not permit an 80% solvent grind and leave enough solvent for the mill wash. This problem can often be overcome by increasing the vehicle solid content of the varnish or resin solutions by some 7-10%. This manipulation frees a considerable amount of solvent for use in the grinding portion without change in the overall paint composition. If this change in varnish concentration is not feasible, grinding may have to be carried out at about 30% binder concentration at some sacrifice in efficiency and output. In this case a new F. P. value for the 30% solution must, of course, be established.

Where the solvent content of the formula is so low that not even 30% vehicle solids can be used, it is questionable if such materials belong in the ball or pebble mill at all. It will usually be found that roller mills or other grinding equipment is more economical to use.

C. *Checks:*

It is well to check the paste in the mill after a few hours' grind to see whether it is still at the F. P. consistency or has changed for some reason or other. At this time it is also practical to measure the consistency by instrument.

The Stormer viscosimeter or the Gardner Mobilometer may be used for this purpose. The consistency of well dispersed pastes at the F. P. is found to correspond to about 80 KU in the Stormer. Careful checks indicate that for high-solvent, high-pigment grinds as used in the F. P. method, best grinding results in the pebble mill are obtained between 70 and 80 KU, and in the ball mill between 80 and 90 KU. This relationship explains the usefulness and significance of the F. P. as a guide to good grind composition.

For vehicles which are poor dispersers or for flocculated pigments which do not produce a sharp F. P., the F. P. values tend to fall below a 70 KU consistency. In such cases the Stormer readings are sometimes a more reliable guide to optimum grind composition than the F. P. values. Yet it is good practice to start out with F. P. formulations and to check the mill paste by instrument for corrections.

If the consistency (at the temperature prevailing in the mill) is below 70 KU, the necessary corrections can be made in subsequent batches. If, on the other hand, the paste viscosity i too high, due to the presence of bodying agents or for othe reasons, further vehicle can be added to the mill batch at once

C. *Discussion of Case Histories:*

It may be well, at this point, to relate and briefly discuss som case histories of the abreviated technique. The examples chose each illustrate certain problems encountered in the applicatio of the basic technique and the methods used to solve thes problems.

EXAMPLE 2:

Pebble Mill Grind of a red enamel, consisting of two pigments, one varnish, one oil, one solvent, and having the following 100 gal. composition:—

42	lbs	Red A
28	"	Red B
83	gal.	Varnish Y (51%)
8	"	Oil
4	"	Solvent
.8	"	Lead Drier
.5	"	Cobalt Drier
101.5	gal.	Theoretical Yield

It is apparent at once that there is not enough solvent in this formula to make a high-solvent grind. Therefore the 51% varnish Y is converted to a 60% varnish. This changes the formula to read 69 gls of varnish Y (60%) and 18 gls of solvent, enough for a high-solvent grind.

A single solution of 20% solids of Varnish Y is prepared and both pigments are titrated with it. The calculations are, of course, simpler than outlined in step 1 of Example 1, but follow the same pattern. Steps 2 and 3 follow exactly the procedure laid down in Example 1. Accordingly, the grind composition is:—

42	lbs	Red A
28	"	Red B
4.9	gal.	Varnish Y (60%)
11.1	"	Solvent
21.2	gal.	Grinding Paste

If the proper charge is, say, 142 gal. the yield of finished paint is $\frac{142}{21.2} \times 101.5 = 680$ gal. 47 gal. of solvent are left for the final mill wash.

Step 4:— A sample drawn after four hours shows a Stormer consistency of 75 KU, hence no vehicle adjustment is needed. Grinding time is eighteen hours.

EXAMPLE 3:

Ball Mill grind of a brown Enamel, consisting of four pigments, one oil, one varnish and one solvent. The varnish has 50% solids and there is only 5 gal. of solvent in 100 gal. of this fairly highly pigmented enamel. Therefore, the 50% varnish is

converted to a 57% varnish. This gives 18.3 gal. of solvent per 100 gal. of finished paint.

After going through Steps 1 and 2 it appears that even with the 57% varnish (S-body) there is not enough solvent available for a concentrate grind. Therefore, Step 1, the F. P. determination, is repeated with a 30% solution and this time there is enough solvent for both the grind and for washing the mill. The Step 3 and 4 procedure follows the previous examples.

EXAMPLE 4:

Pebble Mill grind of an Ivory Enamel, consisting of three pigments, two varnishes and one solvent. The F. P. determination of Step 1 must be made with both varnishes separately. The varnish with the lower F. P. values for the principal pigments is chosen as the grinding vehicle. Otherwise the procedure is the same as outlined in the preceding examples.

EXAMPLE 5:

Pebble Mill grind of a red automotive Enamel, consisting of two alkyds, two solvents and one organic red pigment. A F. P. is obtained in the beaker, but it is clear from the granular appearance of the mix that the pigment is not properly broken down. A pre-grinding operation is necessary to break up the large aggregates before valid F. P.s can be obtained. First, however, a comparative F. P. determination is made with the pigment as is for all possible resin-solvent combinations, namely:

1. Resin A with Solvent X
2. Resin A with Solvent Y
3. Resin B with Solvent X
4. Resin B with Solvent Y

If combination 3 gives the lowest F. P. values, it is selected as the grinding vehicle. A few ounces of this vehicle are placed in a quart can with the amount of pigment indicated by the beaker test and the can is half filled with steel balls. After three or four hours' grinding time, an amount of paste equivalent to 10 grams of the dry pigment is placed in the beaker and more vehicle or vehicle-solvent mixture is added until the F. P. is reached. The total pigment and vehicle concentration is now computed and the procedure of Steps 2 and 3 of the above examples is followed. In Step 4 it is noted that the Stormer consistency of the pebble mill paste is 85 KU and slightly puffy. A few percent additional resin are added to the mill to reduce the consistency to about 80 KU. This reduces the grinding time slightly and facilitates the discharge of the paste from the mill.

The main value of the F. P. methods in this case lies in the determination of the most suitable vehicle for grinding. It is also noted that a cleaner, brighter color and often a better gloss is obtained with grinds of maximum pigment concentration and a high-solvent vehicle, than by grinds with less pigment and more binder.

EXAMPLE 6:

Pebble Mill grind of a white Enamel, containing four lbs of aluminum stearate per 100 gal. The stearate increases the consistency, as indicated by the Stormer. It is therefore necessary to add a small amount of extra vehicle if the consistency range is to be maintained. Generally, about 1 gal. of extra vehicle is required per pound of aluminum stearate. Otherwise the procedure of Example 1 is followed.

EXAMPLE 7:

Pebble Mill grind of a highly pigmented white gloss paint containing three pigments, two oils, one varnish and one solvent. The varnish is a good grinding vehicle, but there is not enough of it and not enough solvent in the formula to serve as the sole grinding liquids. A considerable amount of the oils must be used, but these are very poor dispersers. Hence the paste is very puffy. It grinds slowly and is difficult to discharge from the mill, even if nearly all the liquids are put in the mill. In brief, this is really a roller mill formula. A small percentage of a special chemical dispersant is added to the formula to overcome or at least greatly reduce the flocculation. The F. P. determination must be carried out with the proper proportion of the dispersant in the titration solution. The dispersant permits a much higher pigment concentration to be used, and to make this a suitable formula for pebble mill grinding.

In Step 5 it is found that the paste is still slightly puffy and shows only 65 KU. Disregarding the puffiness, the vehicle portion is reduced in subsequent batches until a consistency of 80 KU is reached.

EXAMPLE 8:

Ball Mill grind of a black alkyd enamel, using Carbolac. Because of the high liquid absorption only 5 gram portions of the black are used for the F. P. determination. Difficulties are encountered in wetting the pigment properly; therefore the pregrinding operation as described in Example 5 is used. The

grinding paste made according to the corrected F. P. value show only 72 KU after twenty hours' grind in ball mill. Hence, th pigment concentration can be increased in subsequent batche Otherwise the procedure of Example 1 is followed.

V. *General Remarks*

(A)

In contract with the ideas propounded in this paper, man production men insist on grinding at high viscosity, sometime as high as 130-140 KU, on the theory that it permits highe pigment loadings and protects the mill against excessive wea

It is true, especially of highly viscous vehicles, that increasin paste consistency permits higher pigment loadings and therefo higher paint output per batch. However, by exceeding the F. range of 80 ± 10 KU, the gain in pigment loading is more tha offset by the extra grinding time required and by the low quality of the paint. The same high pigment concentration the proper paste consistency can be obtained by the use of lo viscosity vehicle and the application of the F. P. technique outlined in this paper.

Regarding mill wear, it has been found that the concentra grinds of the proper consistency show less discoloration in b mills than conventional high KU grinds of comparable finene If discoloration is accepted as a measure of mill wear, as seen logical, a minimum of mill wear seems to take place in conce trate grinds. This may be due partly to the shorter grindi time and partly to the greater role of the inter-particle shear.

(B)

It should be mentioned here that the new grinding method, exchange for the greater output, demands somewhat more tention and greater accuracy in plant operation. Batch siz are rather narrowly prescribed. Errors in mill loadings w show up and so will changes in the qualities of the major co ponents. In this sense the new method may be said to be mo sensitive than the conventional grinding practice. It is sensiti enough, in fact, to be utilized as a procedure for raw mater control. Some plants have adopted the method for this purpo They check the vehicle against one standard batch of some pi ment, and the pigments against one standard batch of a sta vehicle. Faulty cooks which cannot be easily discovered viscosity determinations may show up distinctly in the F. values.

VI. *Summary*

A procedure is described for determining the optimum grinding composition for ball and pebble mills. The binder/solvent ratio and the binder/pigment ratio are lower and the total pigment concentration higher than in conventional grinding formulae. The advantages of this method are:

1. More output per mill
2. Improved grinds, or shorter grinding time
3. Greater uniformity of finished product
4. Less discoloration; more brilliant colors
5. More complete color development

The method has been successfully used in paint plants for the past three years.

Acknowledgement

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APPENDIX B

SILICA GRINDING

MILL CALIBRATION OF SILICA

WATER CONTENT 0.09%, INITIAL BET-SURFACE AREA 0.127 m^2/g

Sample Kg

Time = o hr

um	%passing
300	100
300-212	97.1
212-147	82.6
147-106	55.8
106-74	18.2
74-63	2.0
53-45	0.5
45	0.2

MILL CALIBRATION OF SILICA
WATER CONTENT 0.09%, INITIAL BET-SURFACE AREA 0.127 m^2/g

Sample 1.5 Kg
Time = 1/4 hr

um	mesh	% passing
+300	+48	100
300-212	48-65	99.7
212-147	65-100	95.1
147-106	100-150	79.8
106-74	150-200	40.7
74-53	200-270	21.0
53-45	270-325	14.8
45	-325	10.0

MILL CALIBRATION OF SILICA

WATER CONTENT 0.09%, INITIAL BET-SURFACE AREA 0.127 m^2/g

Sample 1.5 Kg
Time = 1/2 hr

um	mesh	% passing
+300	+48	100
300-212	48-65	99.93
212-147	65-100	98.64
147-106	100-150	90.32
106-74	150-200	59.42
74-53	200-270	37.04
53-45	270-325	27.5
45	-325	18.23

MILL CALIBRATION OF SILICA
WATER CONTENT 0.09%, INITIAL BET-SURFACE AREA 0.127 m^2/g

Sample 1.5 Kg
Time = 1.0 hr

um	mesh	% passing
+300	+48	100
300-212	48-65	100
212-147	65-100	99.85
147-106	100-150	97.32
106-74	150-200	82.66
74-53	200-270	58.74
53-45	270-325	46.10
45	-325	30.34

MILL CALIBRATION OF SILICA

WATER CONTENT 0.09%, INITIAL BET-SURFACE AREA 0.127 m^2/g

Sample 1.0 Kg
Time = 1/4 hr

um	mesh	% passing
+300	+48	100
300-212	48-65	99.47
212-147	65-100	94.84
147-106	100-150	81.82
106-74	150-200	44.36
74-53	200-270	23.63
53-45	270-325	16.93
45	-325	11.25

MILL CALIBRATION OF SILICA
WATER CONTENT 0.09%, INITIAL BET-SURFACE AREA 0.127 m^2/g

Sample 1.0 Kg
Time = 1/2 hr

um	mesh	% passing
+300	+48	100
300-212	48-65	100
212-147	65-100	99.6
147-106	100-150	95.5
106-74	150-200	74.4
74-53	200-270	49.3
53-45	270-325	38.1
45	-325	25.4

MILL CALIBRATION OF SILICA
WATER CONTENT 0.09%, INITIAL BET-SURFACE AREA 0.127 m^2/g

Sample 1.0 Kg
Time = 1 hr

um	mesh	% passing
+300	+48	100
300-212	48-65	100
212-147	65-100	99.98
147-106	100-150	99.82
106-74	150-200	99.28
74-53	200-270	91.31
53-45	270-325	78.63
45	-325	56.10

MILL CALIBRATION OF SILICA

WATER CONTENT 0.09%, INITIAL BET-SURFACE AREA 0.127 m^2/g

Sample 0.5 Kg
Time = 1/4 hr

um	mesh	% passing
+300	+48	100
300-212	48-65	100
212-147	65-100	100
147-106	100-150	99.8
106-74	150-200	96.9
74-53	200-270	82.9
53-45	270-325	59.1
45	-325	46.4

MILL CALIBRATION OF SILICA
WATER CONTENT 0.09%, INITIAL BET-SURFACE AREA 0.127 m^2/g

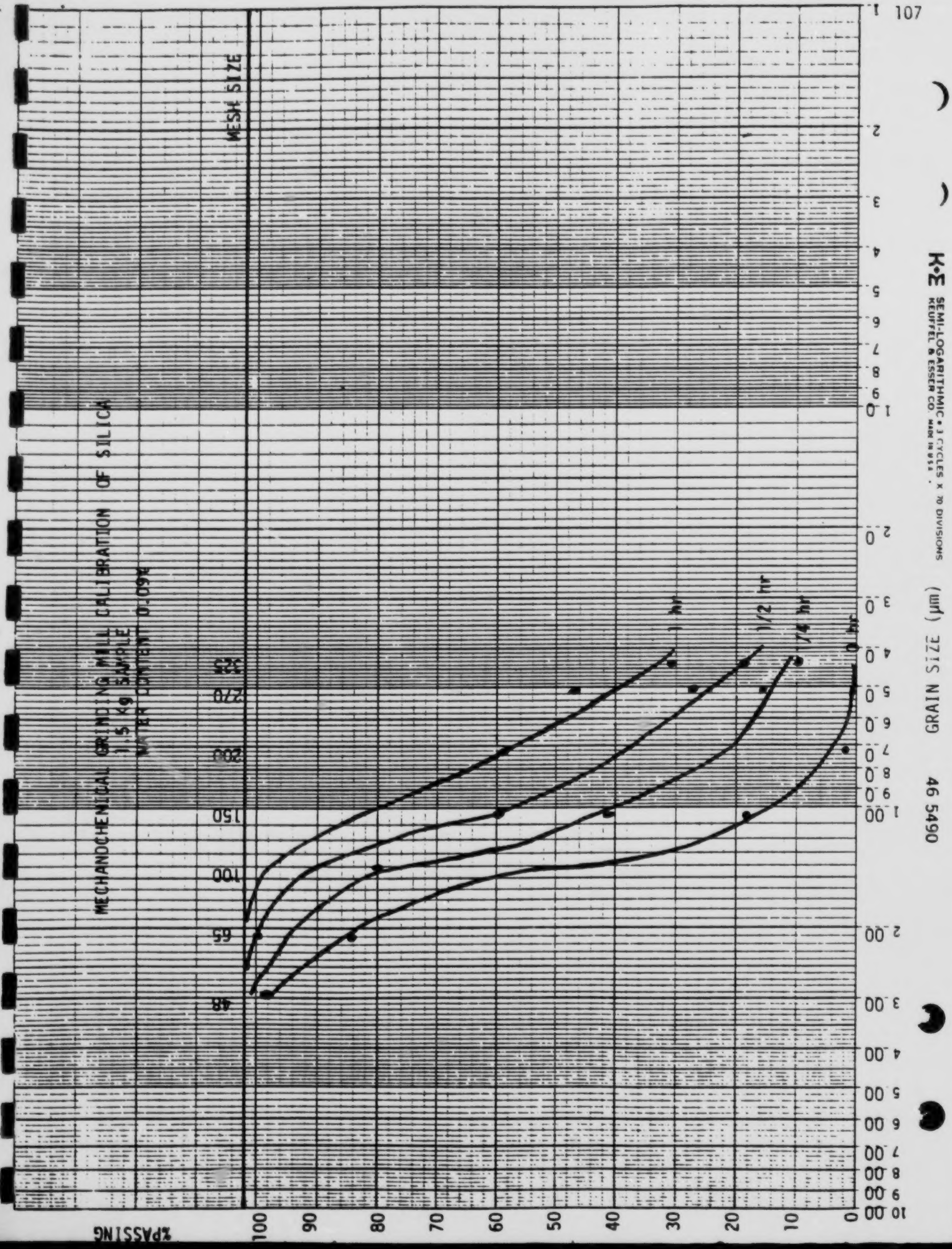
Sample 0.5 Kg
Time = 1/2 hr

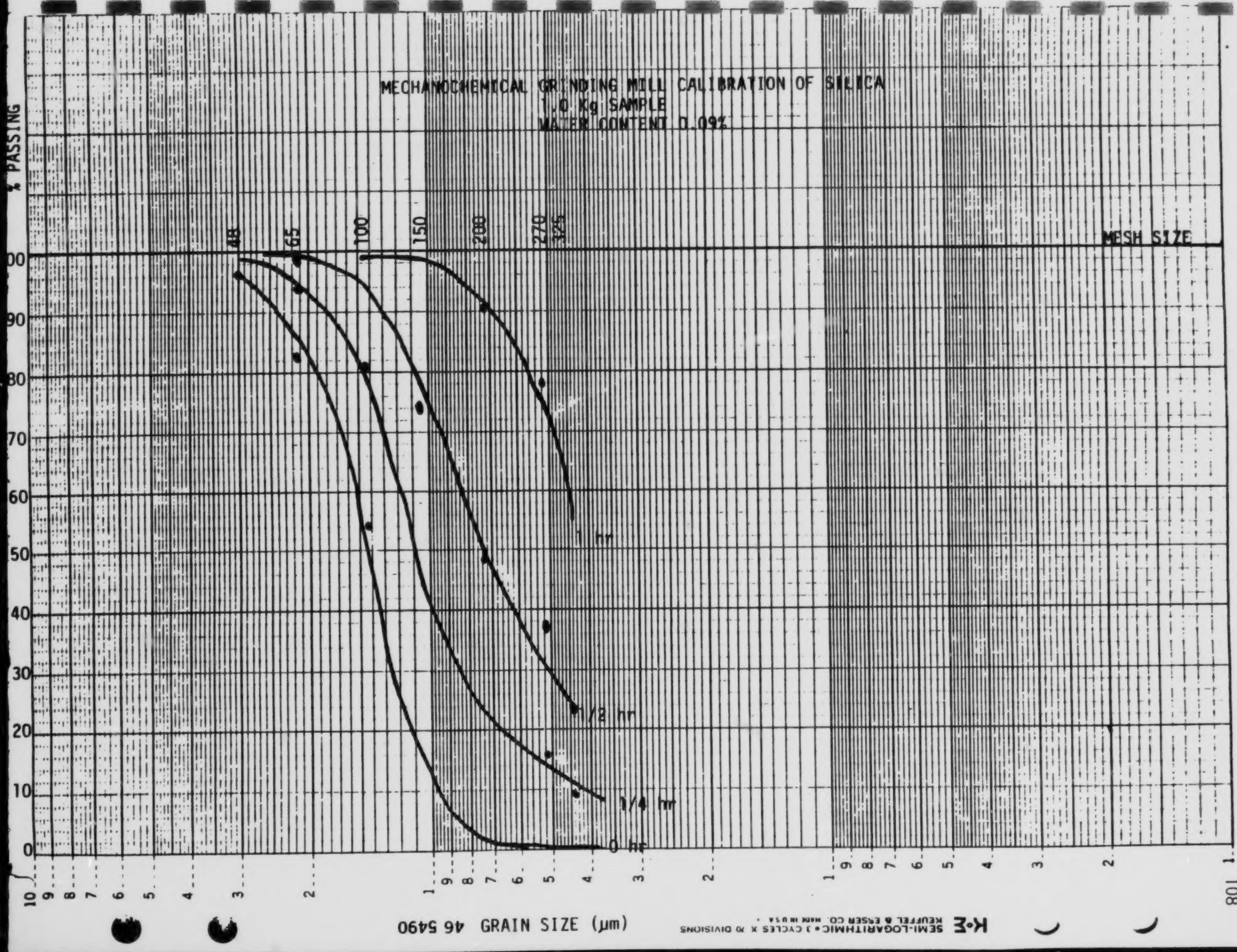
um	mesh	% passing
+300	+48	100
300-212	48-65	100
212-147	65-100	100
147-106	100-150	100
106-74	150-200	99.88
74-53	200-270	94.76
53-45	270-325	84.85
45	-325	67.70

MILL CALIBRATION OF SILICA
WATER CONTENT 0.09%, INITIAL BET-SURFACE AREA 0.127 m^2/g

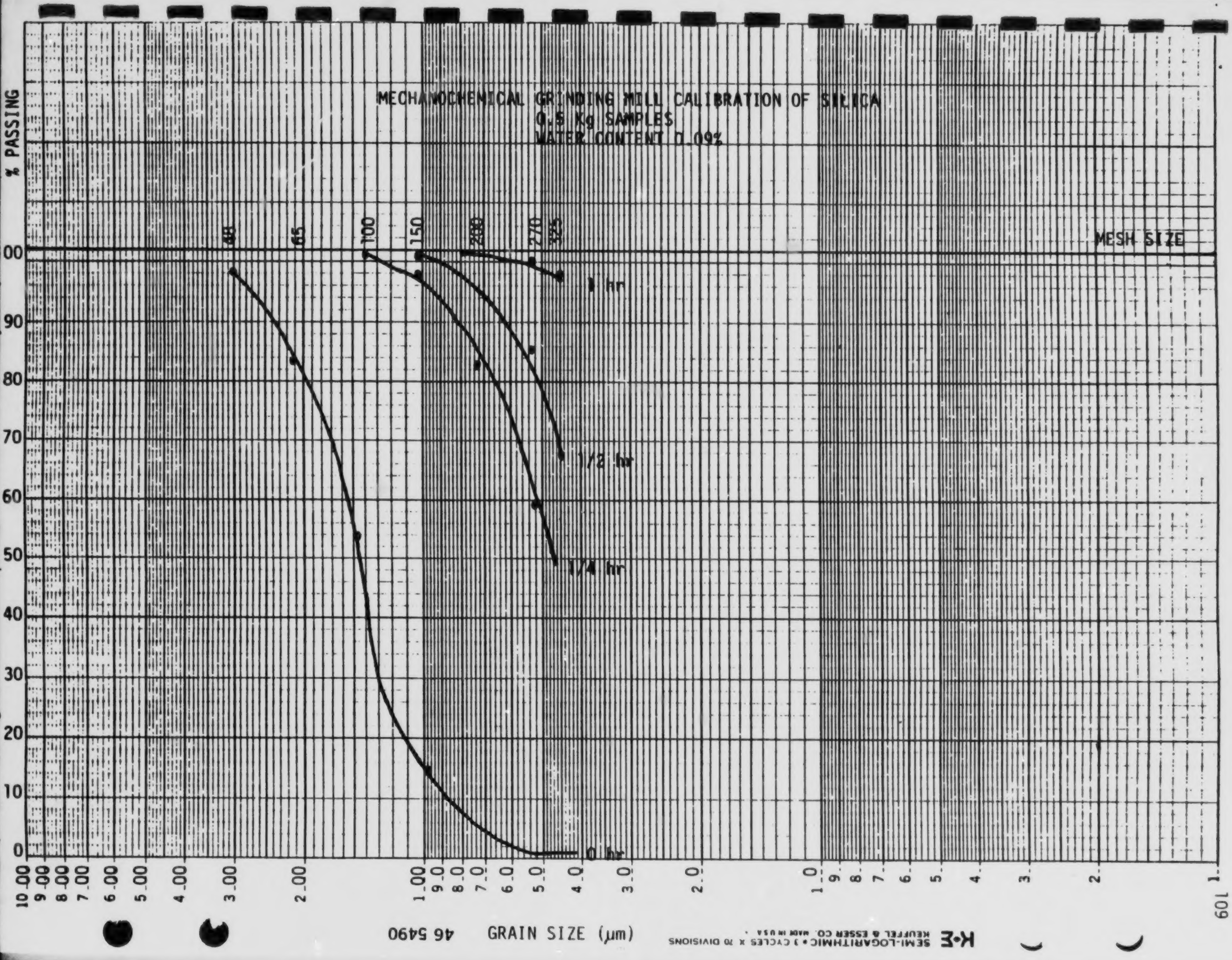
Sample 0.5 Kg
Time = 1 hr

um	mesh	% passing
+300	+48	100
300-212	48-65	100
212-147	65-100	100
147-106	100-150	99.9
106-74	150-200	99.8
74-53	200-270	99.6
53-45	270-325	99.2
45	-325	96.9

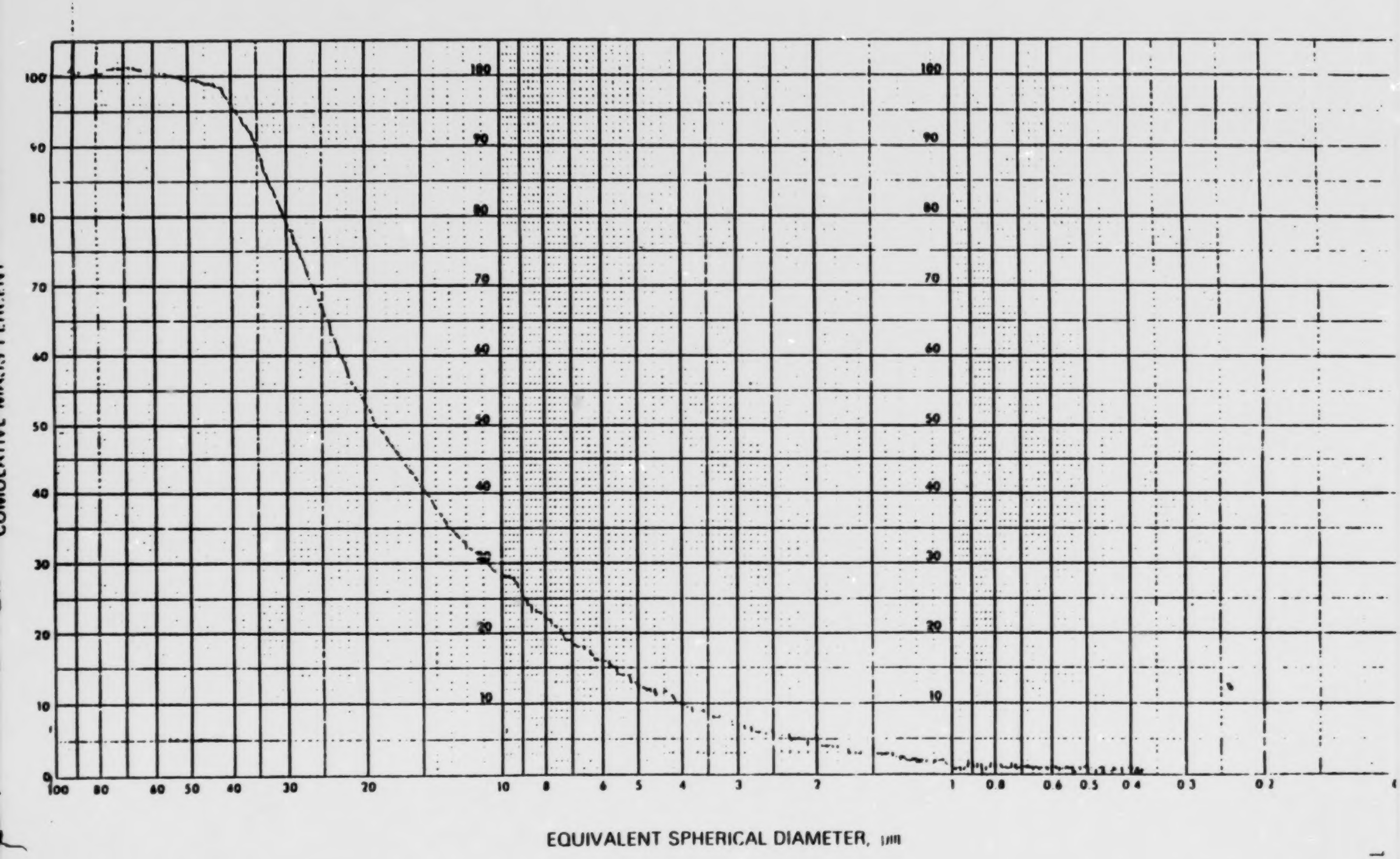

MECHANOCHEMICAL GRINDING MILL CALIBRATION OF SILICA
1.5 Kg SAMPLE
WATER CONTENT 0.09%
MESH SIZE
325
270
200
150
100
65
48
1 hr
1/2 hr
1/4 hr
0 hr
%PASSING
100
90
80
70
60
50
40
30
20
10
0
GRAIN SIZE (μm)
1
2
3
4
5
6
7
8
9
10
20
30
40
50
60
70
80
90
100
200
300
400
500
600
700
800
900
1000
46 5490
K+E SEMI-LOGARITHMIC • 3 CYCLES X 70 DIVISIONS
KEUFFEL & ESSER CO. MADE IN U.S.A.



MECHANOCHEMICAL GRINDING MILL CALIBRATION OF SILICA
1.0 Kg SAMPLE
WATER CONTENT 0.09%


MECHANOCHEMICAL GRINDING MILL CALIBRATION OF SILICA
0.5 Kg SAMPLES
WATER CONTENT 0.09%
% PASSING
100
90
80
70
60
50
40
30
20
10
0
MESH SIZE
48
65
100
150
200
270
325
1 hr
1/2 hr
1/4 hr
0 hr
10.00
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
9
8
7
6
5
4
3
2
1
GRAIN SIZE (μm)
46 5490
K•E SEMI-LOGARITHMIC • 3 CYCLES X 70 DIVISIONS
KEUFFEL & ESSER CO. MADE IN U.S.A.

Calibration grind/silica/1.5 Kg/ 1/4 hr/fraction - 45 µm/sedigraph analysis



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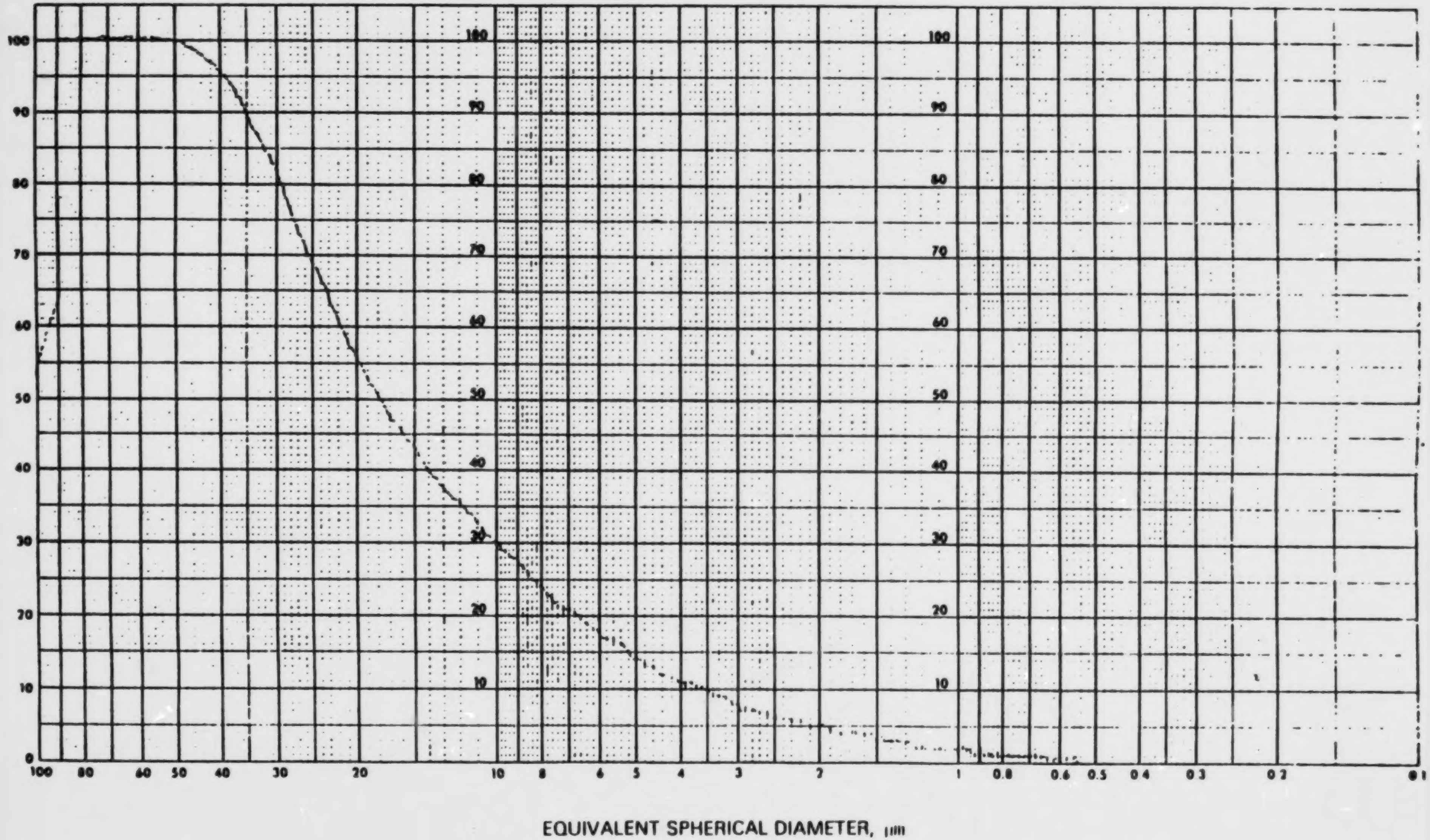
instrument corporation

Calbriation grind/silica/1.5 Kg/ 1/2 hr/fraction -45 µm/sedigraph analysis



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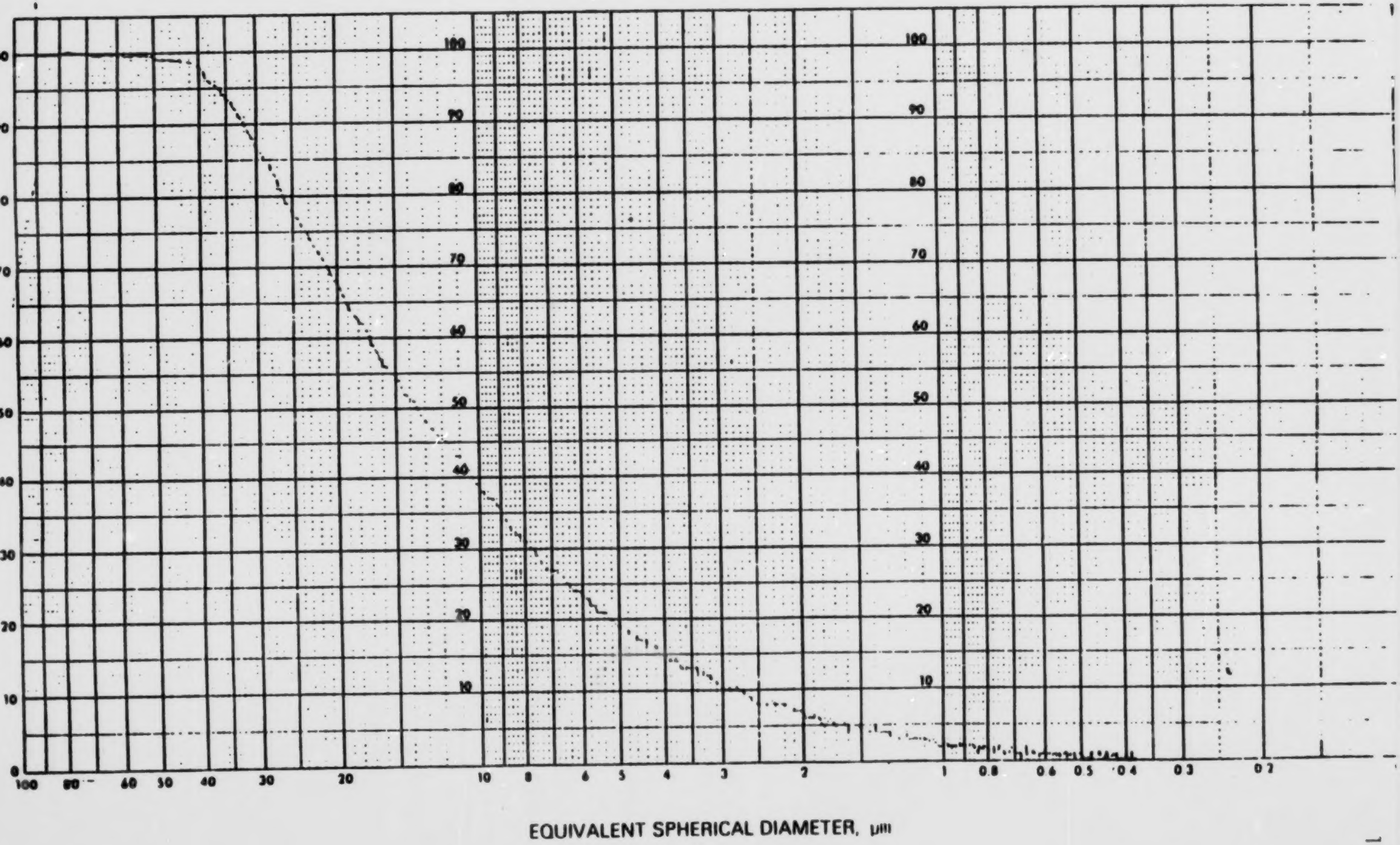
Calibration grinding/silica/1.5 Kg/ 1 hr/fraction -45 µm/sedigraph analysis



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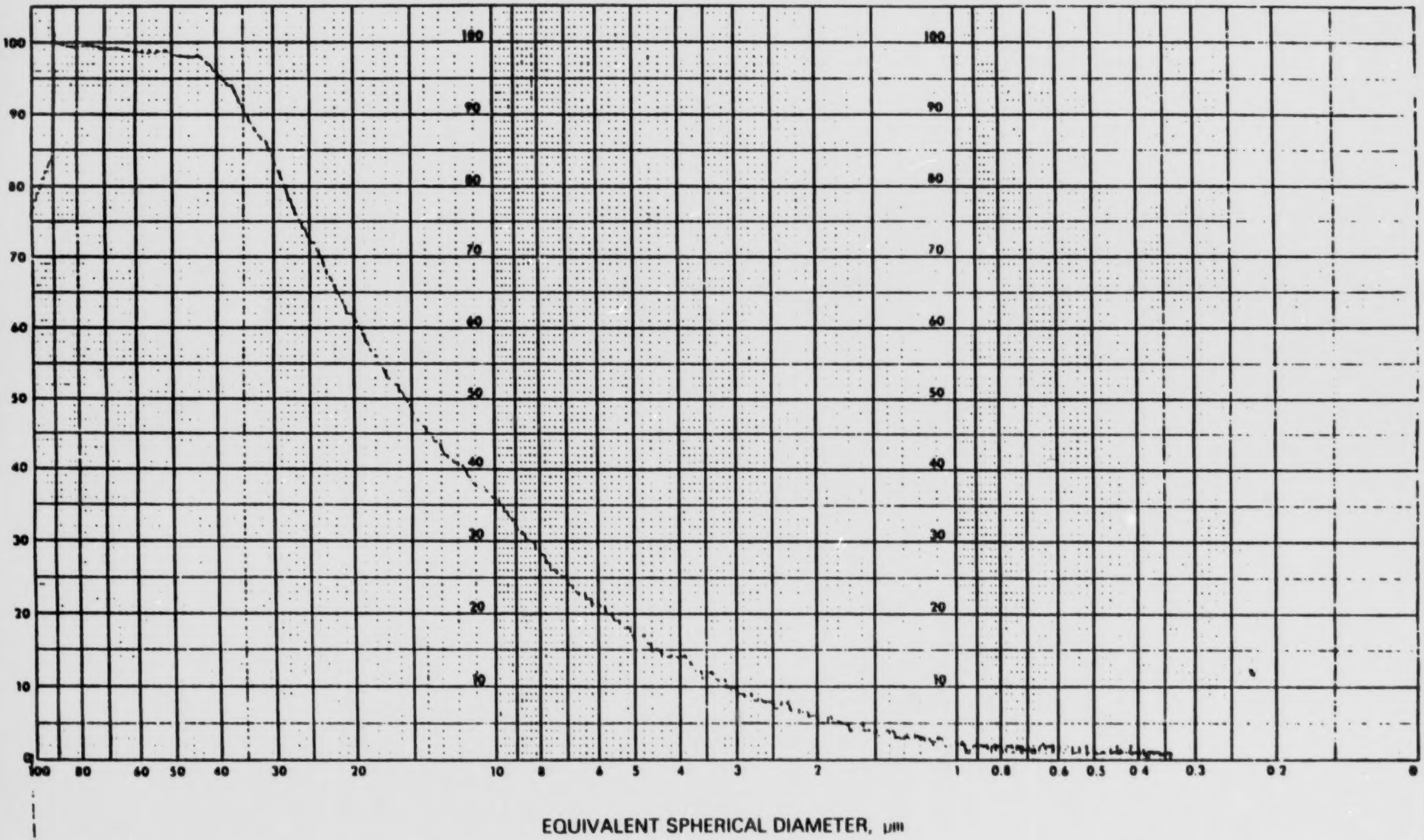
Calibration grinding/silica/1 Kg/ 1/4 h/fraction -45 µm/sedigraph analysis



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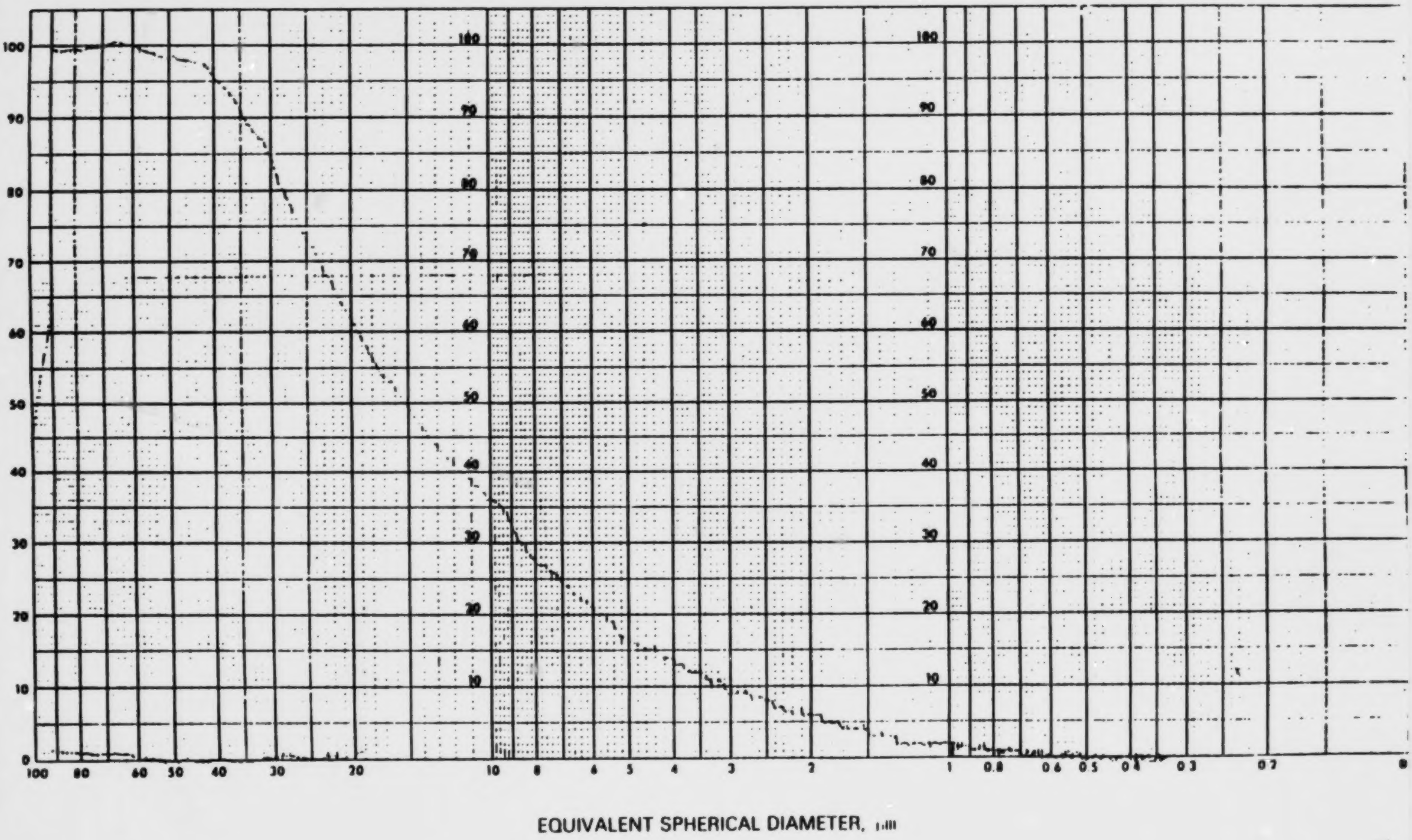
Calibration grinding/silica/1 Kg/ 1/2 h/fraction -45 µm/sedigraph analysis



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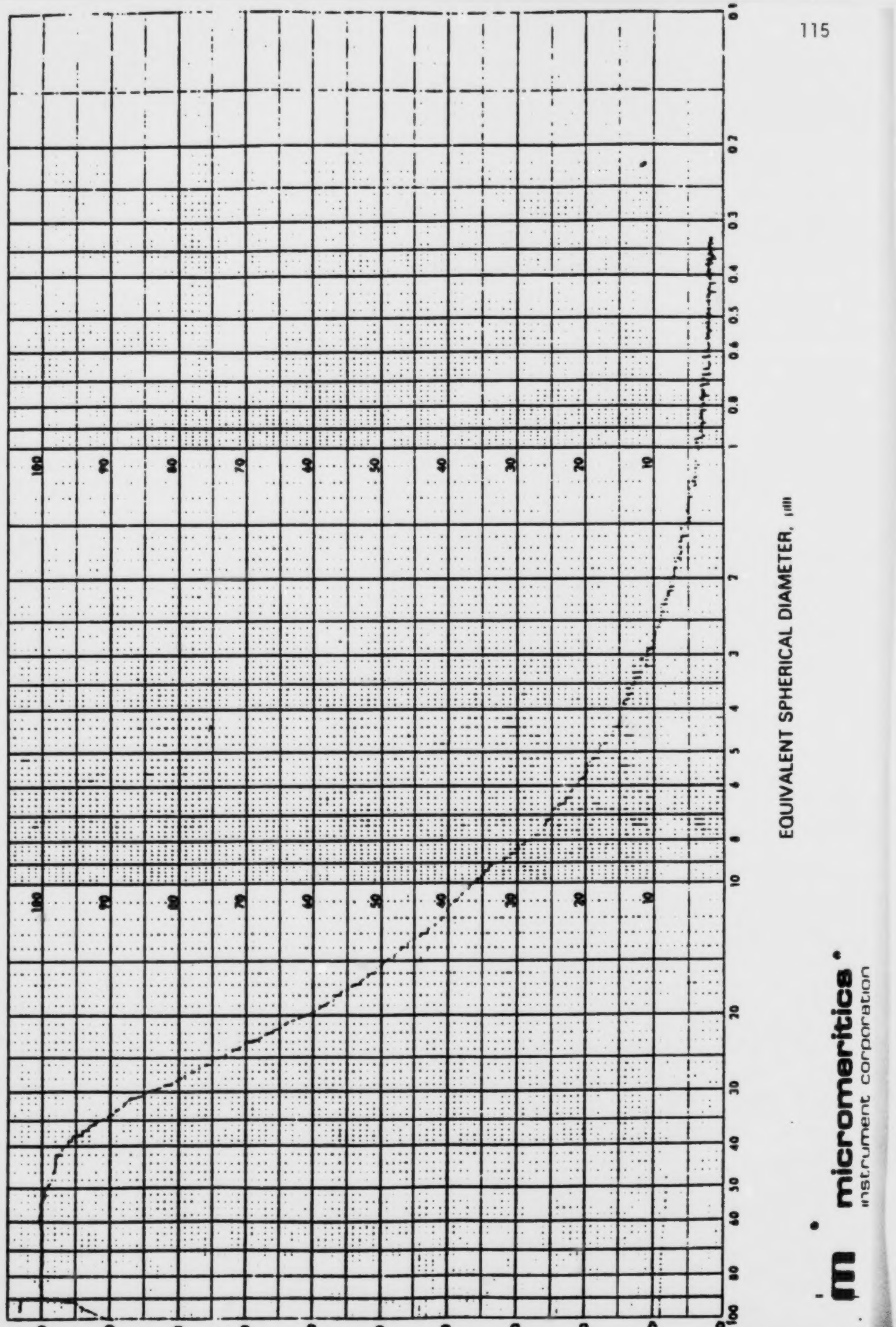
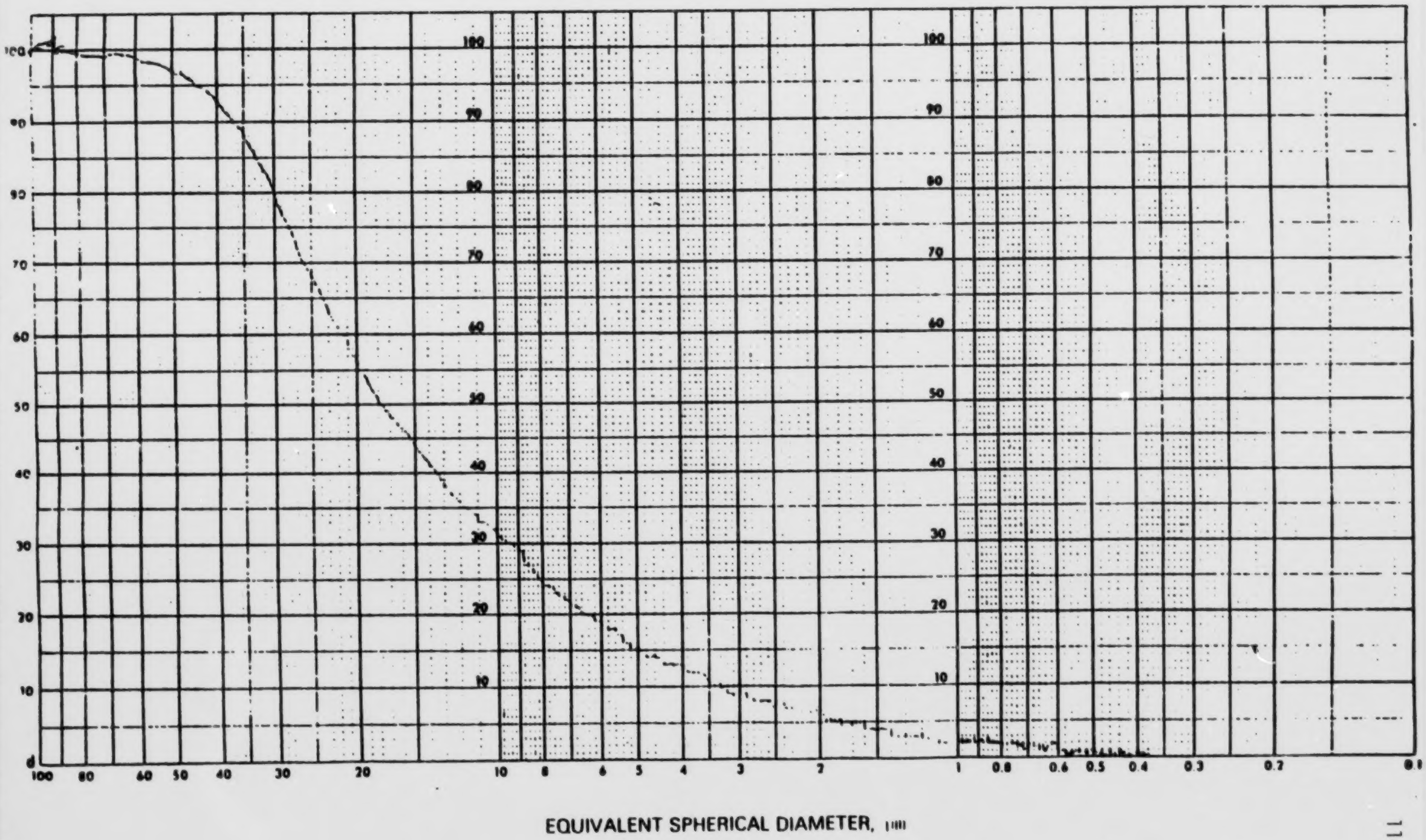
Calibration grinding/silica/1 Kg/1 h/fraction -45 µm/sedigraph analysis



PARTICLE SIZE DISTRIBUTION

Calibration grinding/silica/0.5 Kg/ 1/4 h/fraction -45 µm/sedigraph analysis



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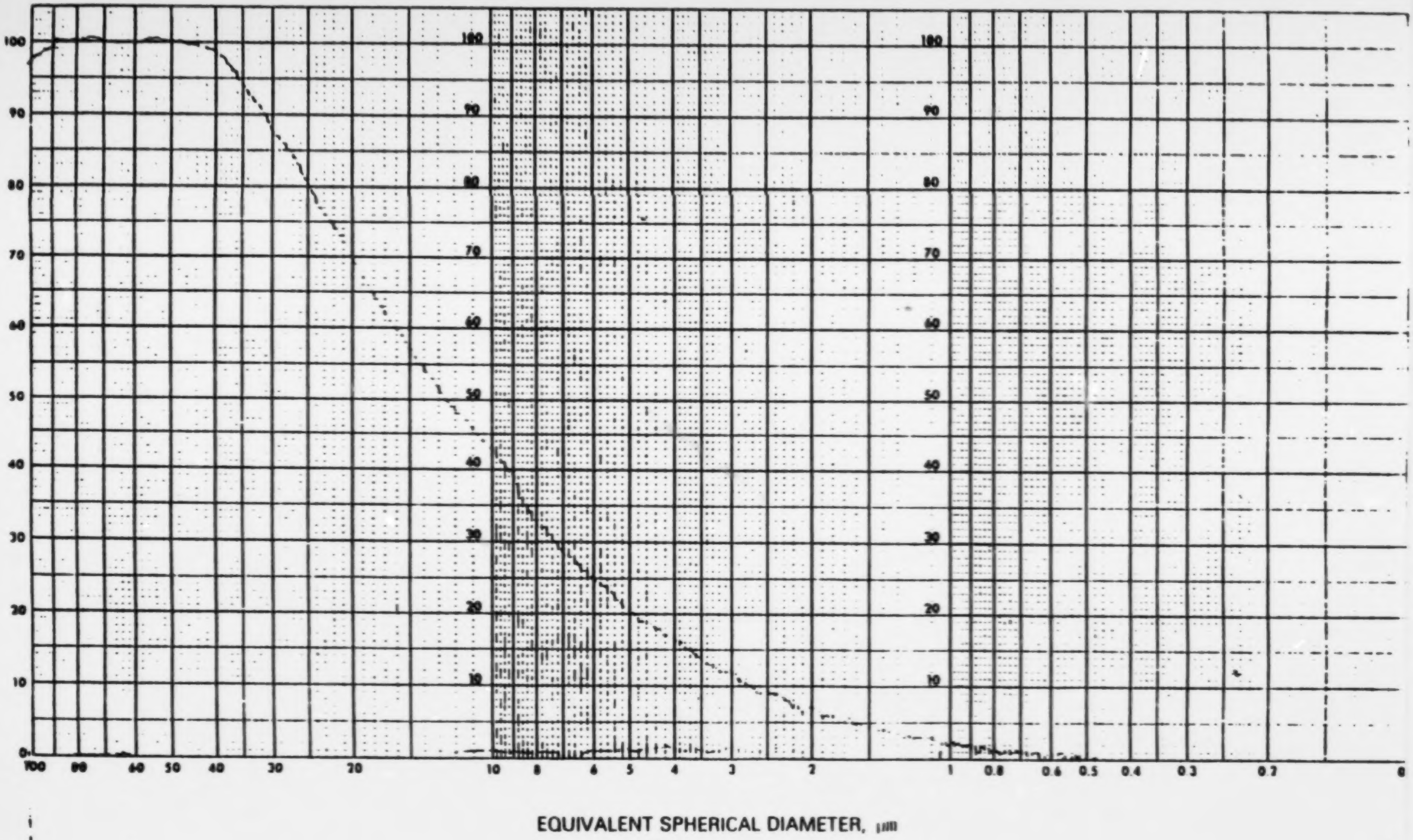
6. Calibration grinding/silica/0.5 Kg/ 1/2 h/fraction -45 µm/sedigraph analysis



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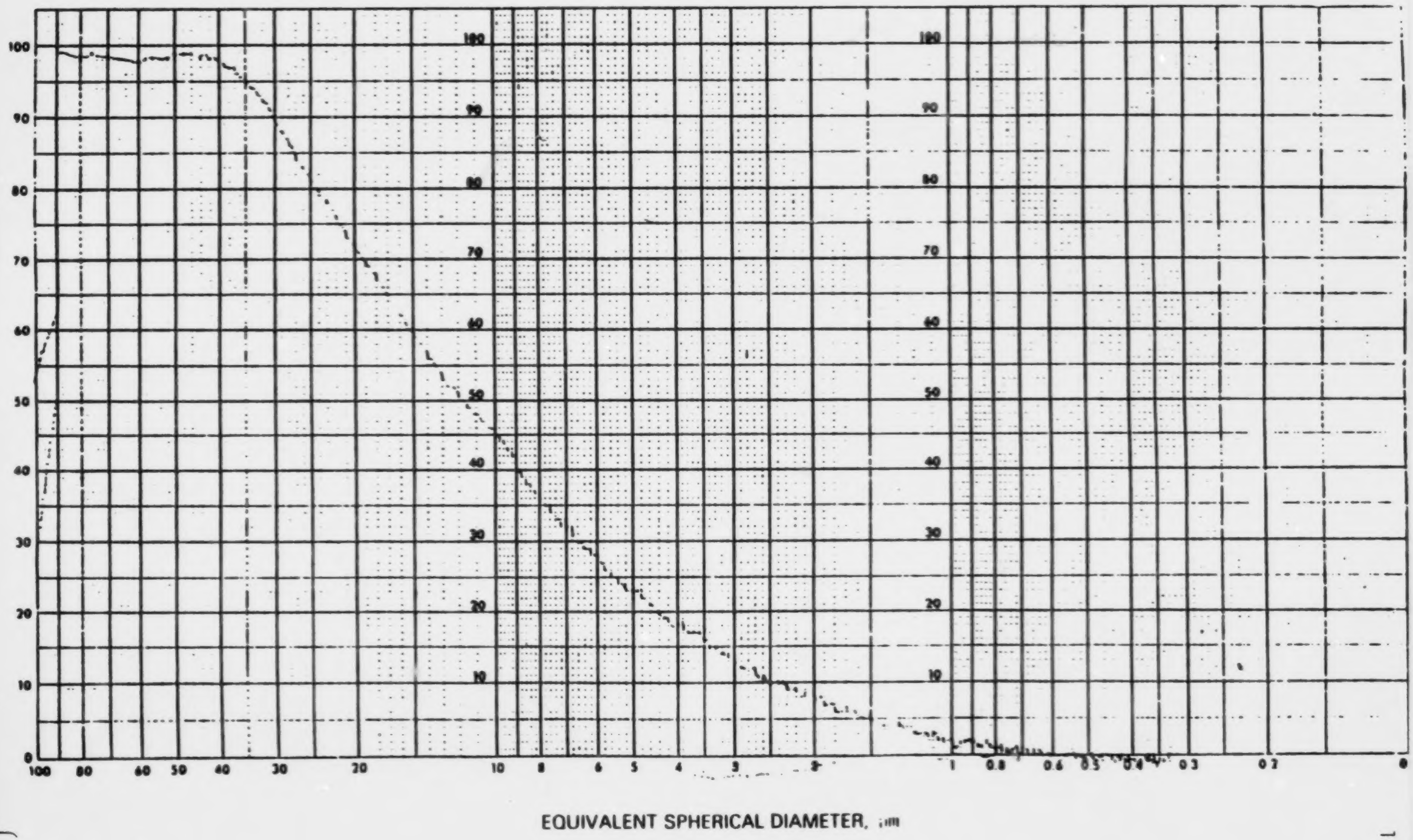
instrument corporation

Calibration grinding/silica/0.5 Kg/ 1 h/fraction -45 µm/sedigraph analysis



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Selected Standard Silica Grind

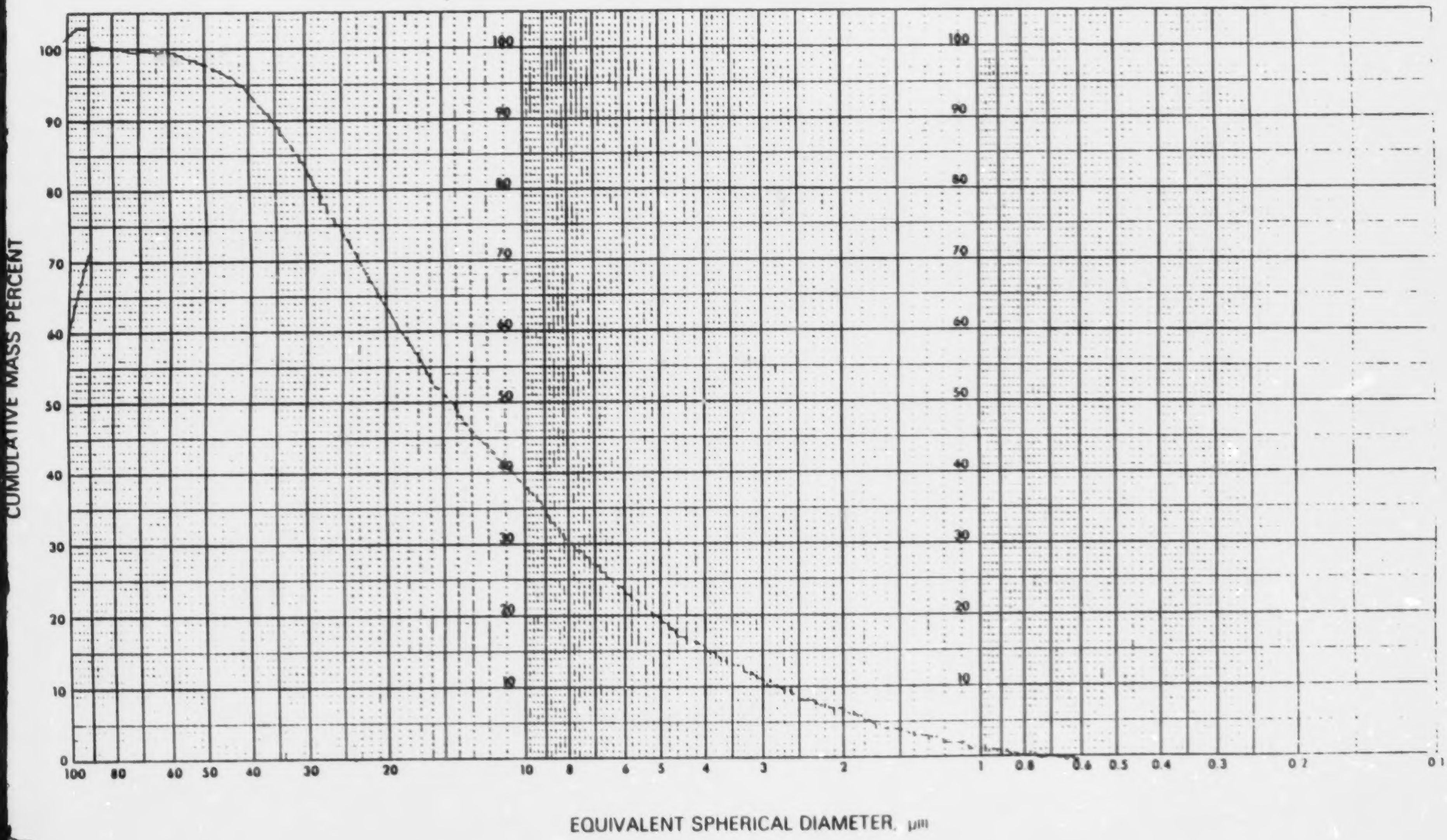
Moisture content = 0.09%

Feed Charge = 750g

Time = 90 min

% Particle Passing	Particle Size
100	45 um
97.1	45.38 um
87.4	38 um

Organic grinding/silica/90 min/0.75 kg/blank/Sedigraph analysis



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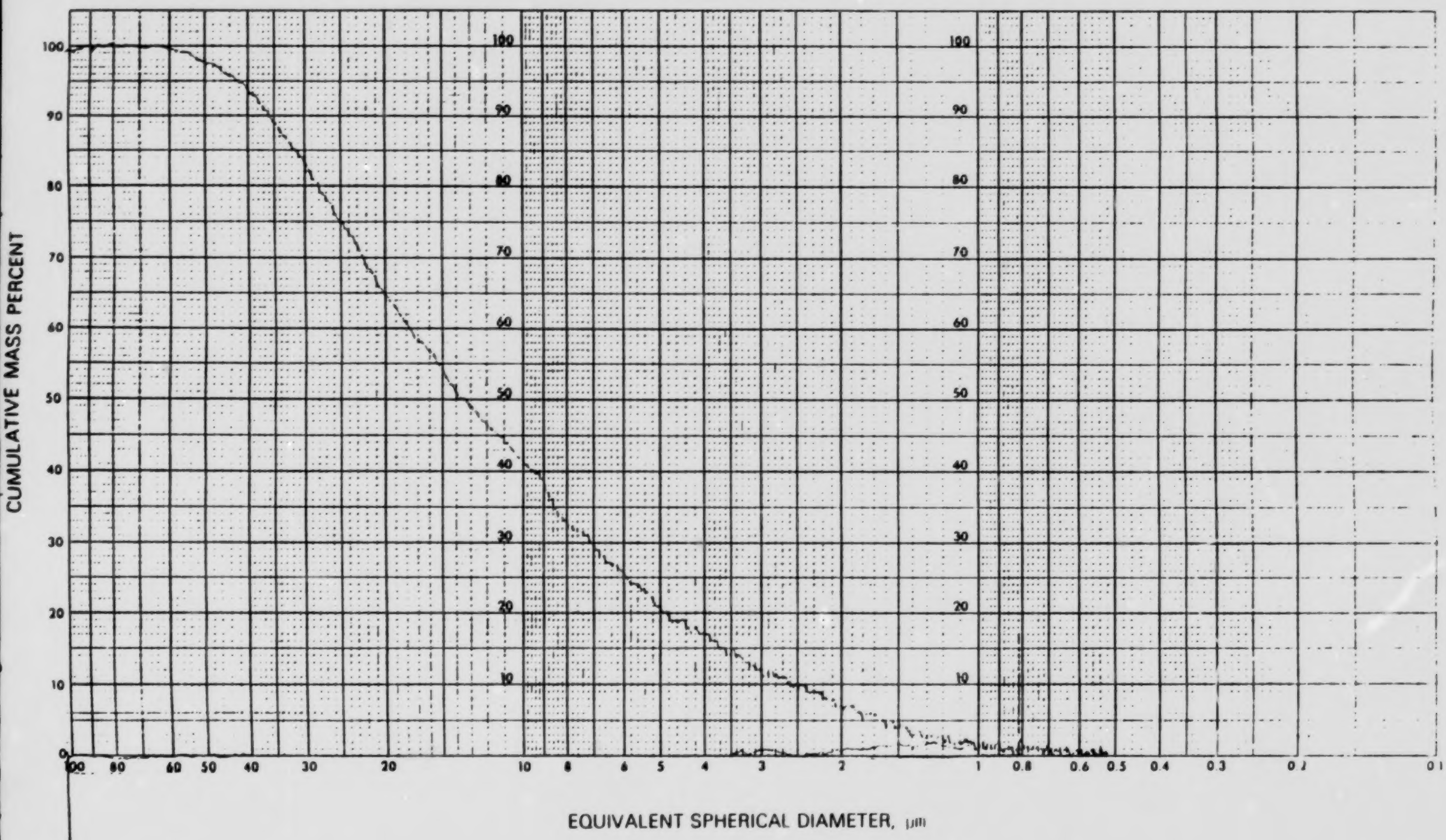
Organic grinding/silica/90 min/0.75 kg/propionic acid (3 g/kg)/sedigraph analysis



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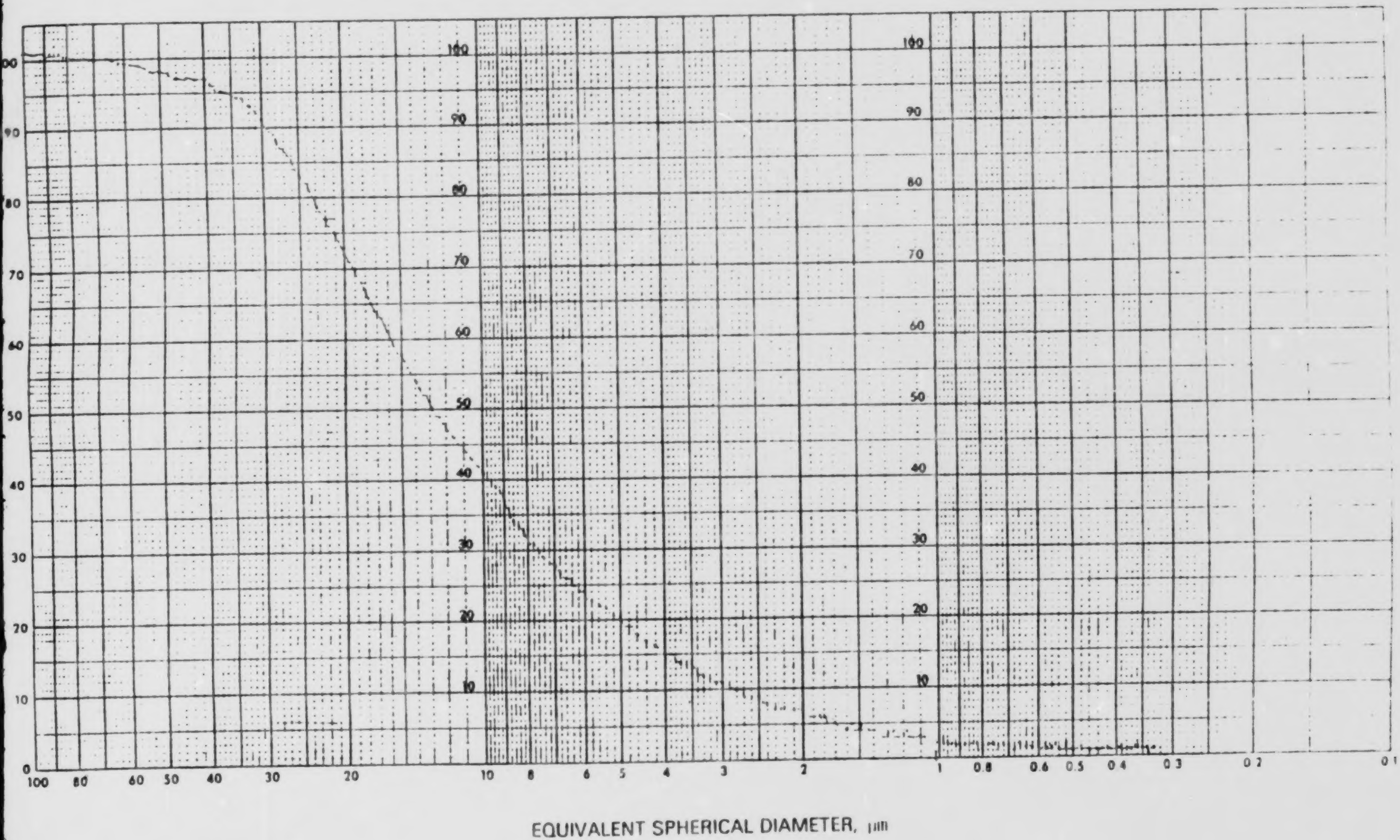
Organic grinding/silica/37.5% H_2O/propanol (3 g/kg)/sedigraph analysis



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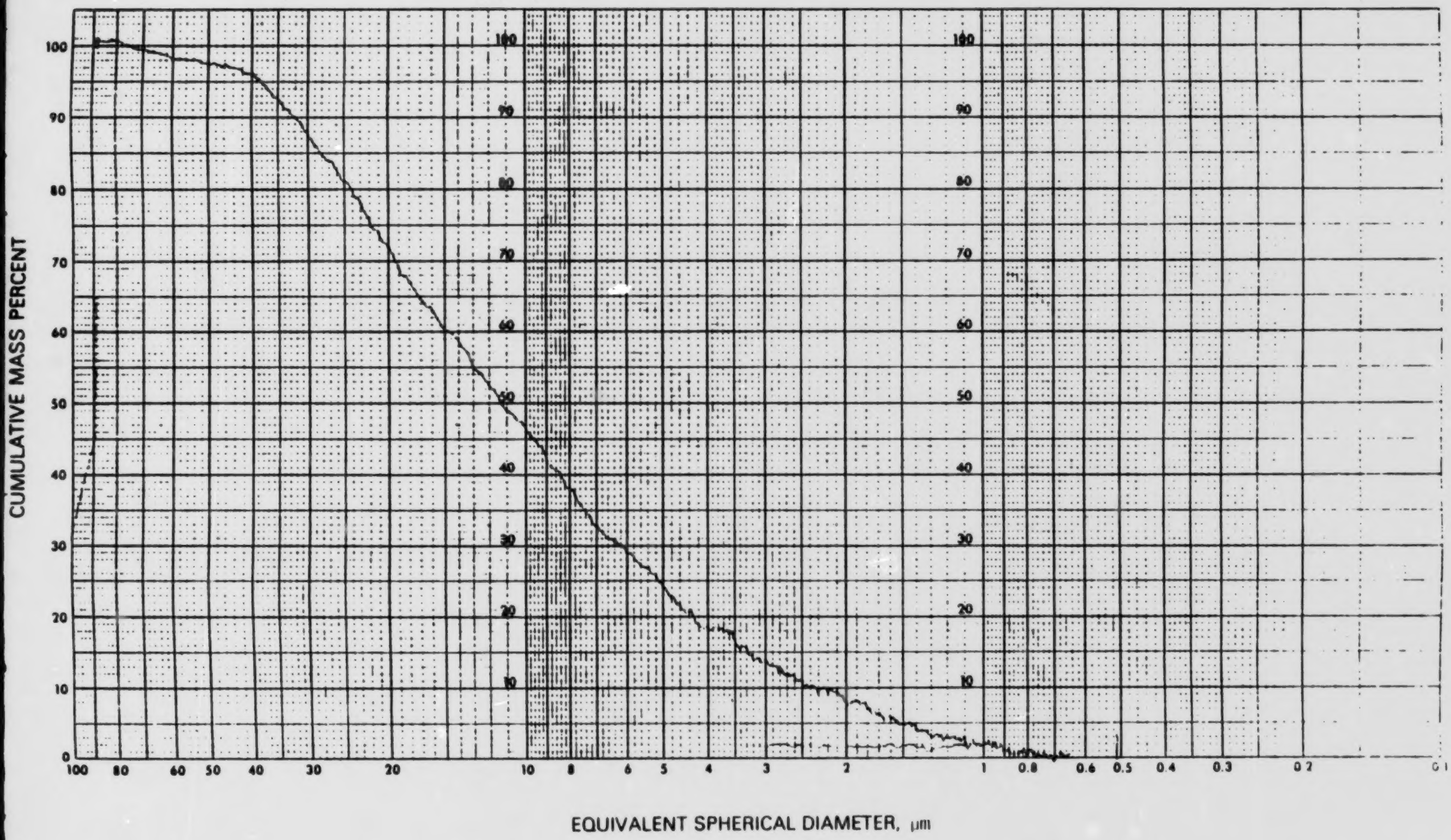
Organic grinding/silica/90 min/0.75 kg/propanol (3 g/kg)/sedigraph analysis



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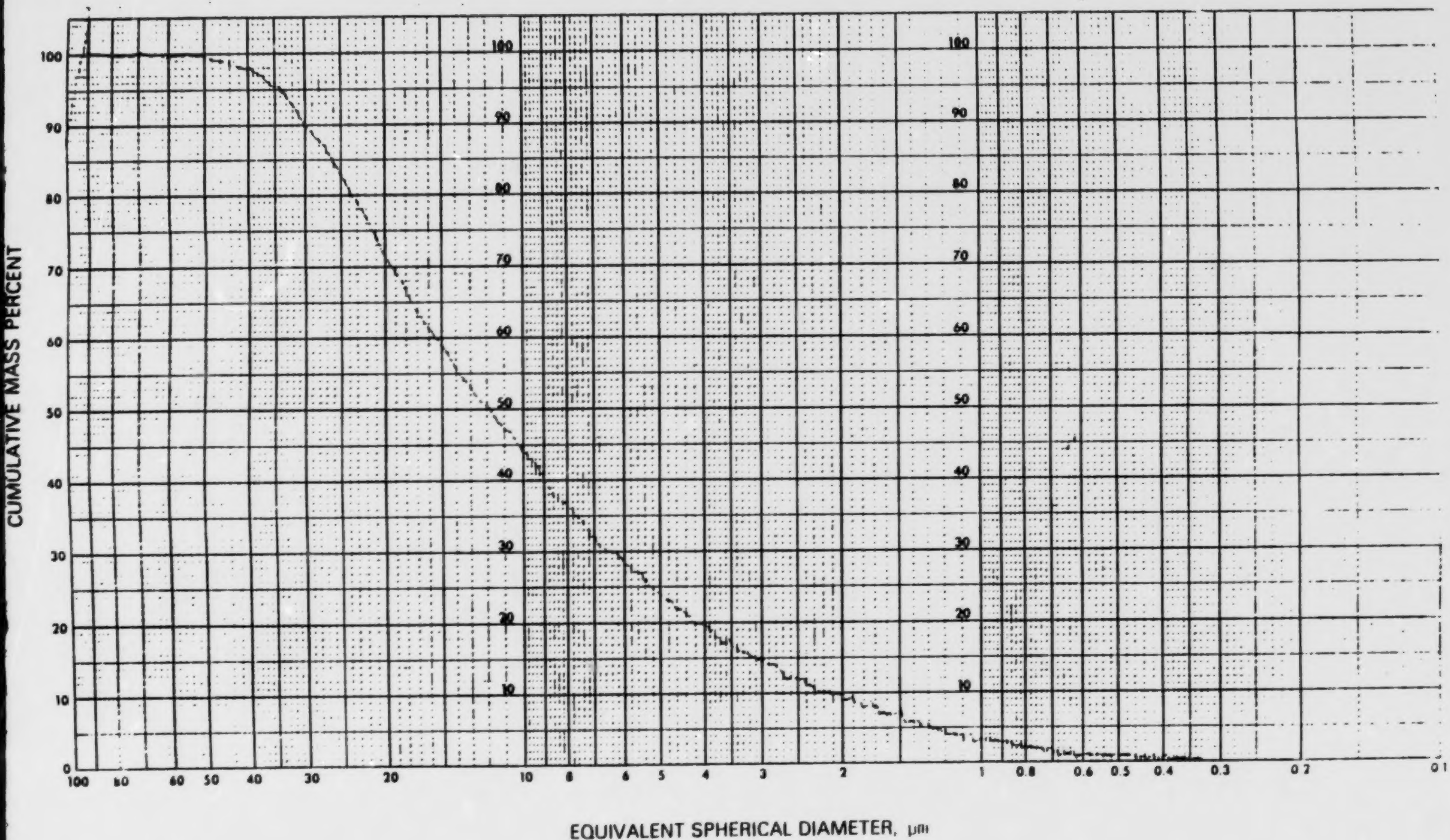
Organic grinding/silica/90 min/0.75 kg/ether (3 g/kg)/sedigraph analysis



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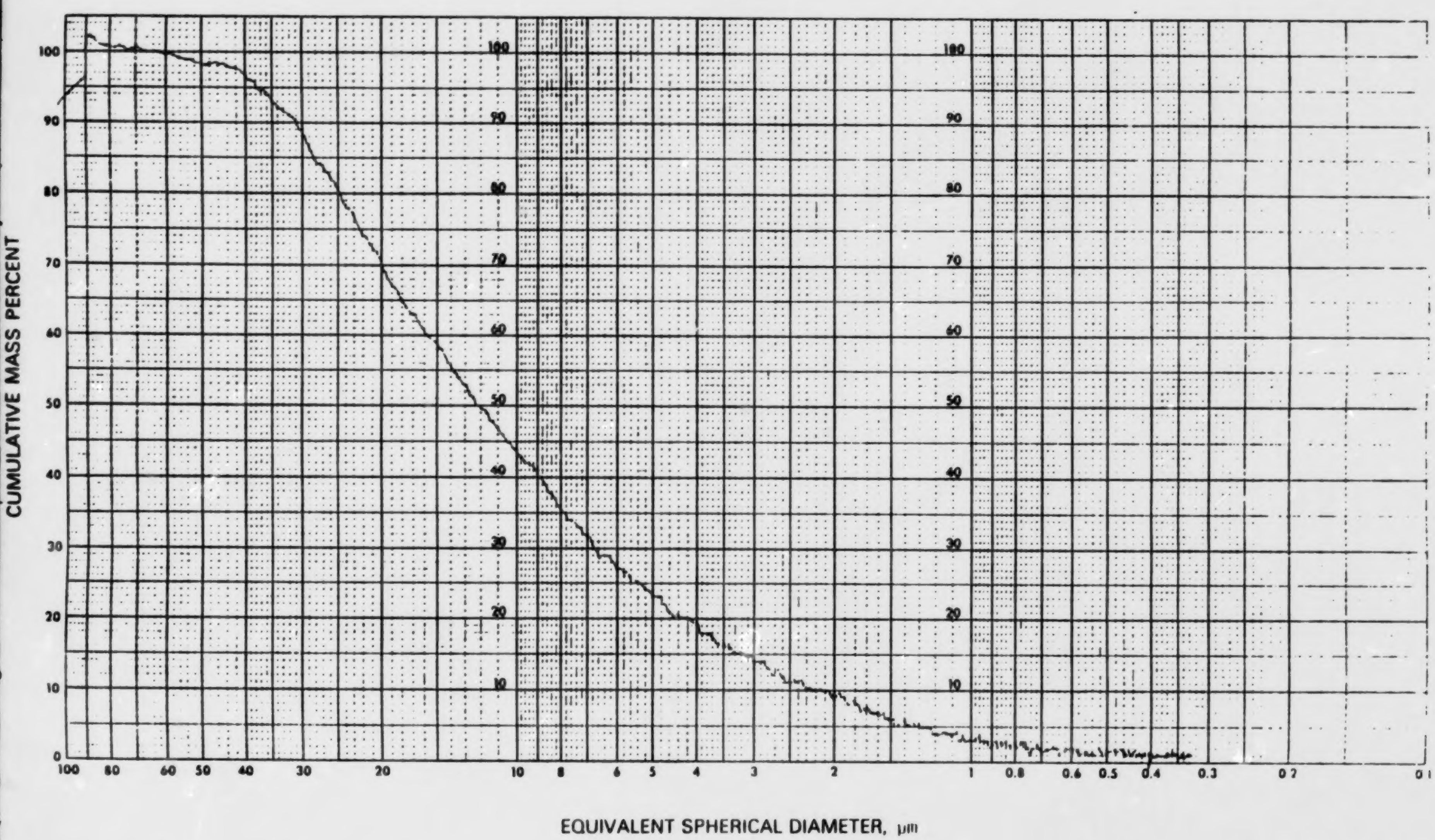
Organic grinding/silica/90 min/0.75 kg/ketone (3 g/kg)/sedigraph analysis



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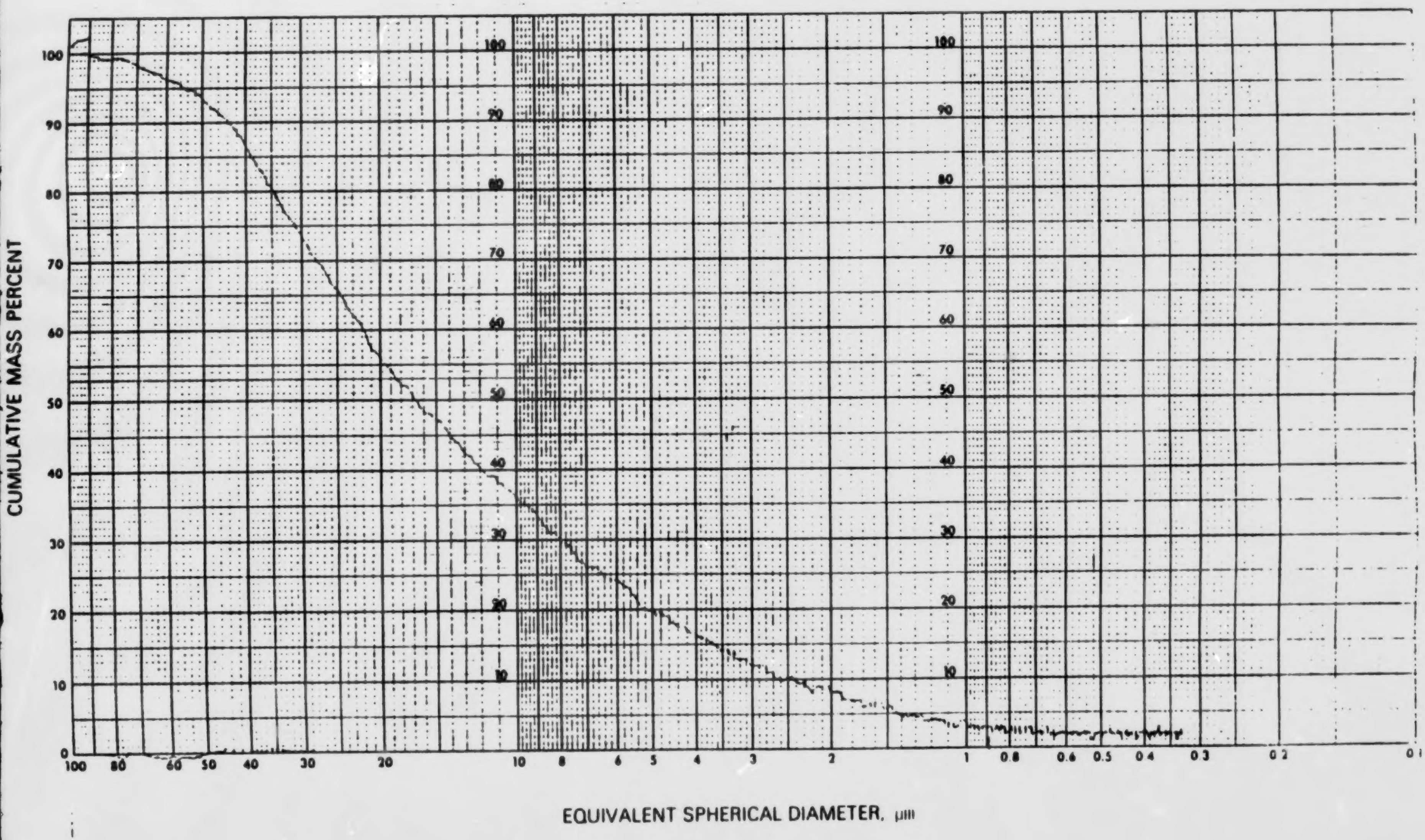
Organic grinding/silica/90 min/0.75 kg/kerosene (3 g/kg)/sedigraph analysis



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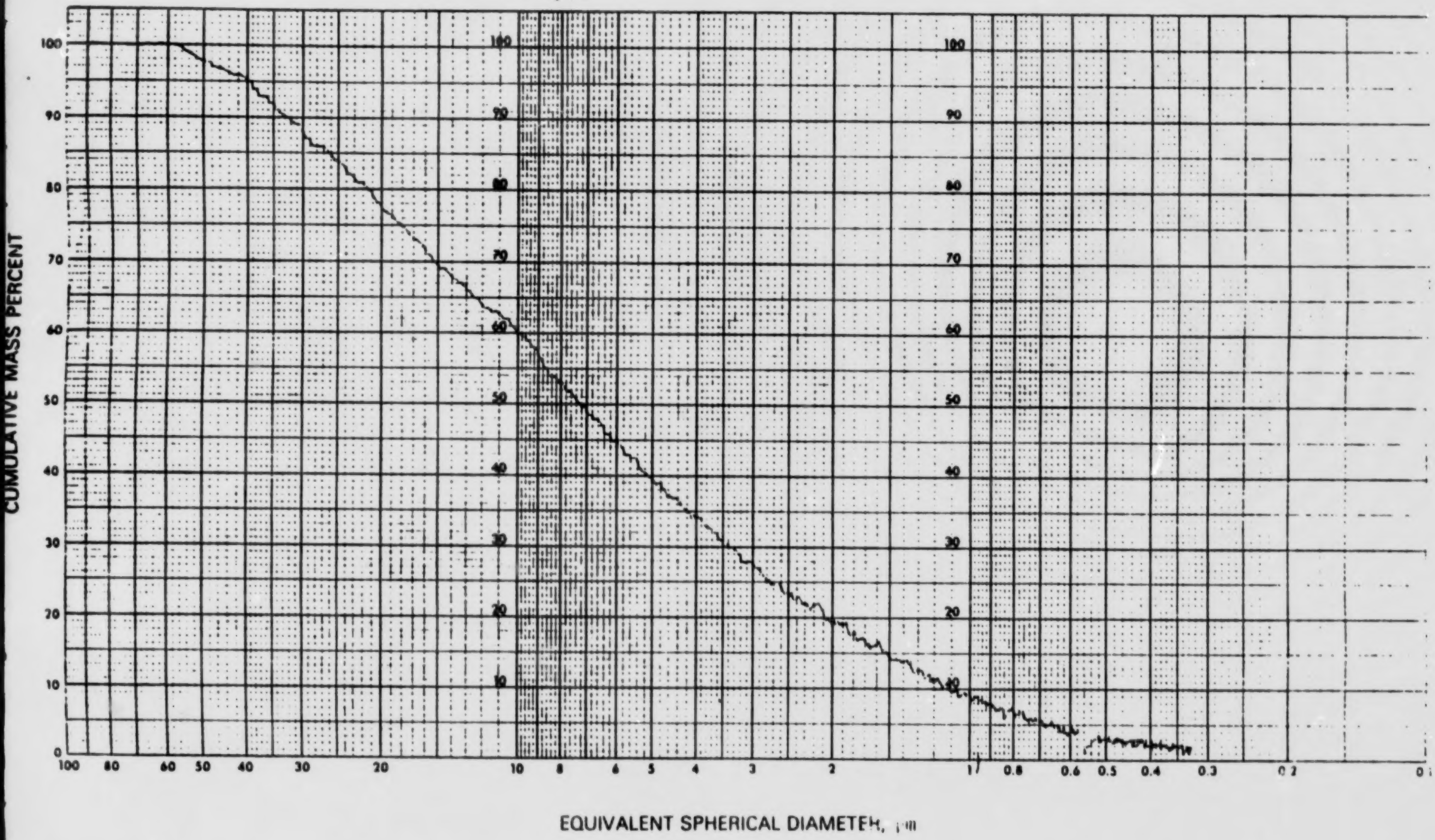
Organic grinding/silica/vibratory disc mill/blank/sedigraph analysis



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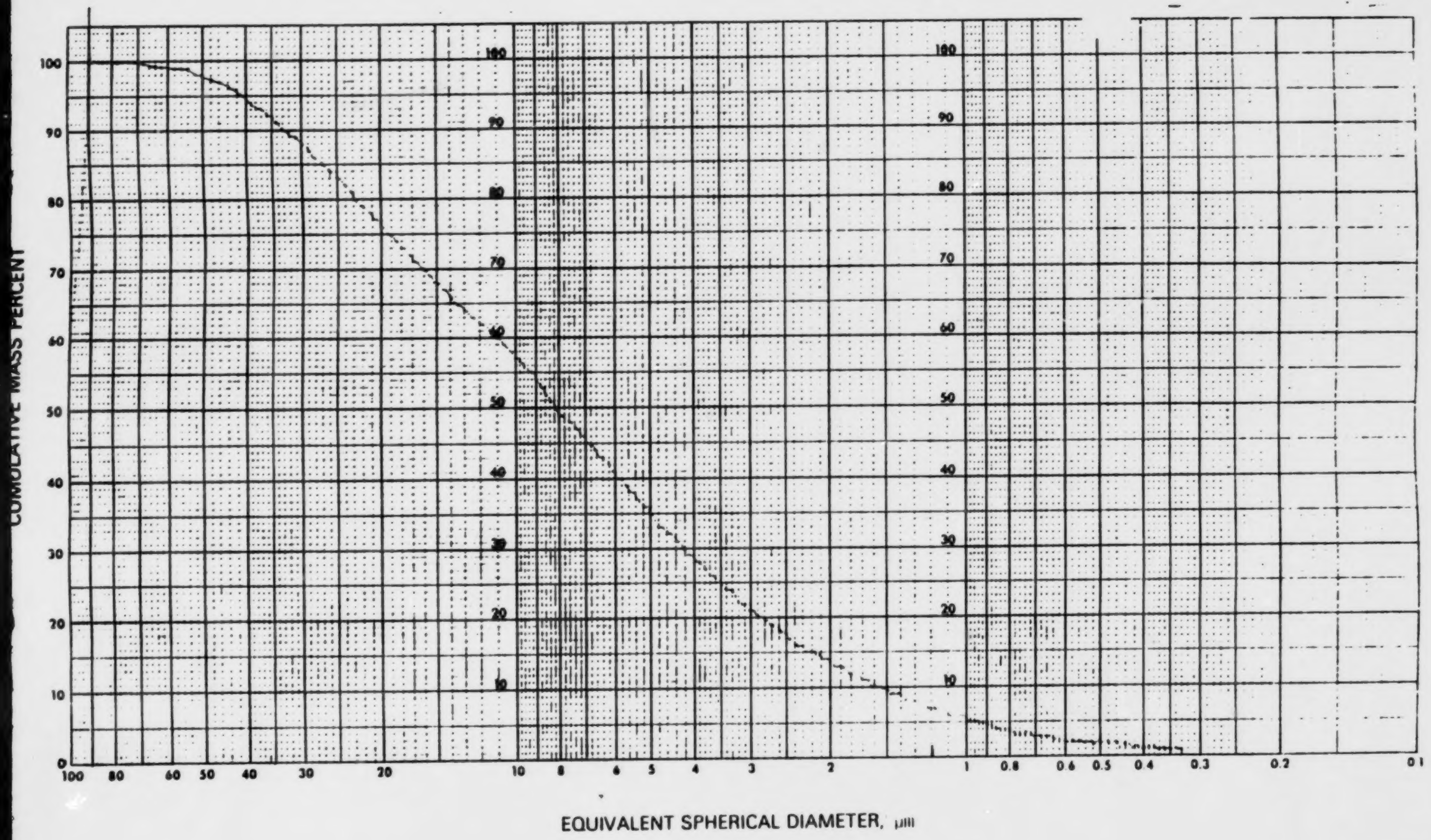
Organic grinding/silica/vibratory disc mill/propanol (10 g/kg)/sedigraph analysis



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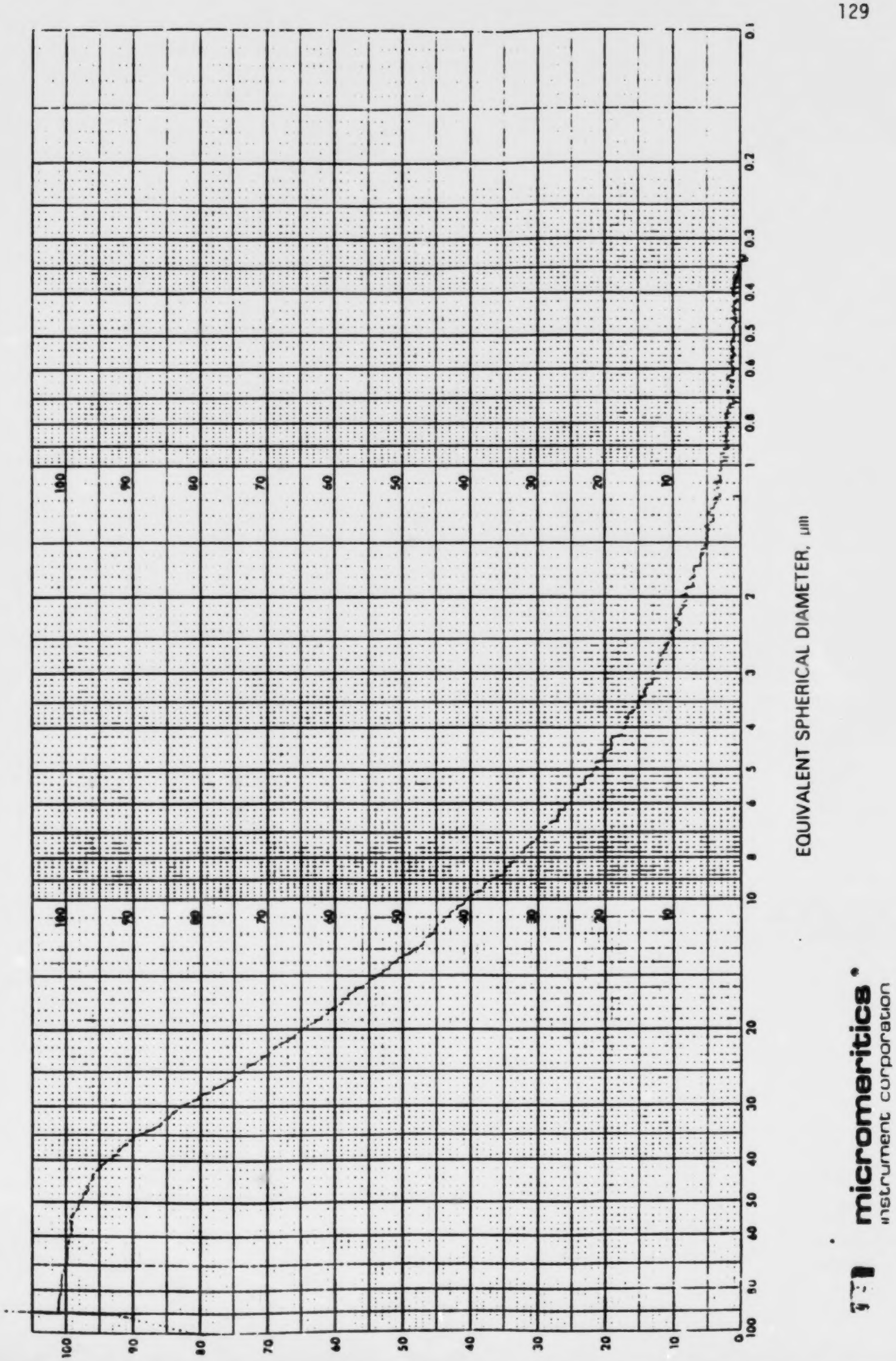
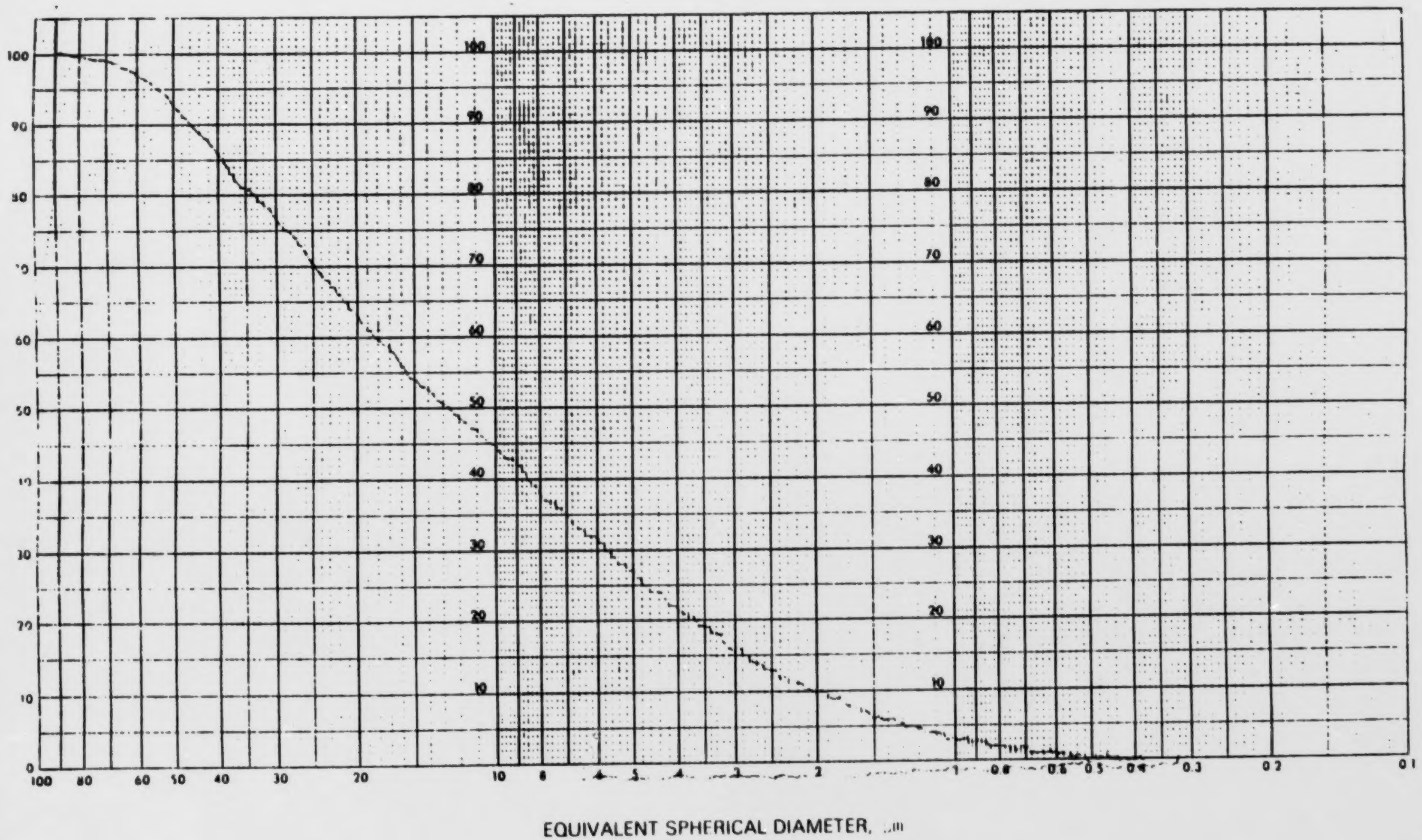
Organic grinding/silica/0.0% H_2O/blank/sedigraph analysis



Organic grinding/silica/10% H_2O/blank/sedigraph analysis



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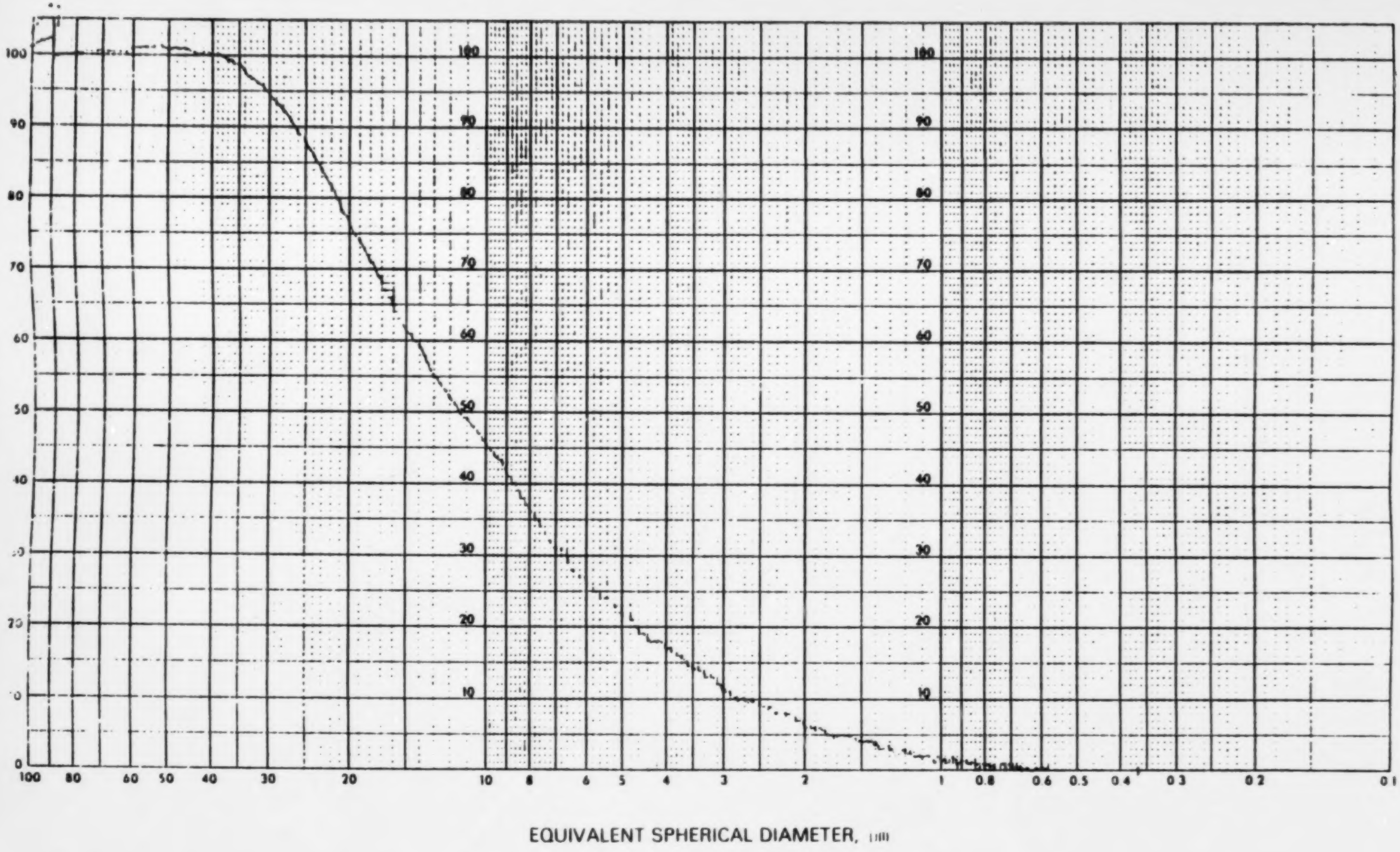
Organic grinding/silica/25% H_2O/blank/sedigraph analysis



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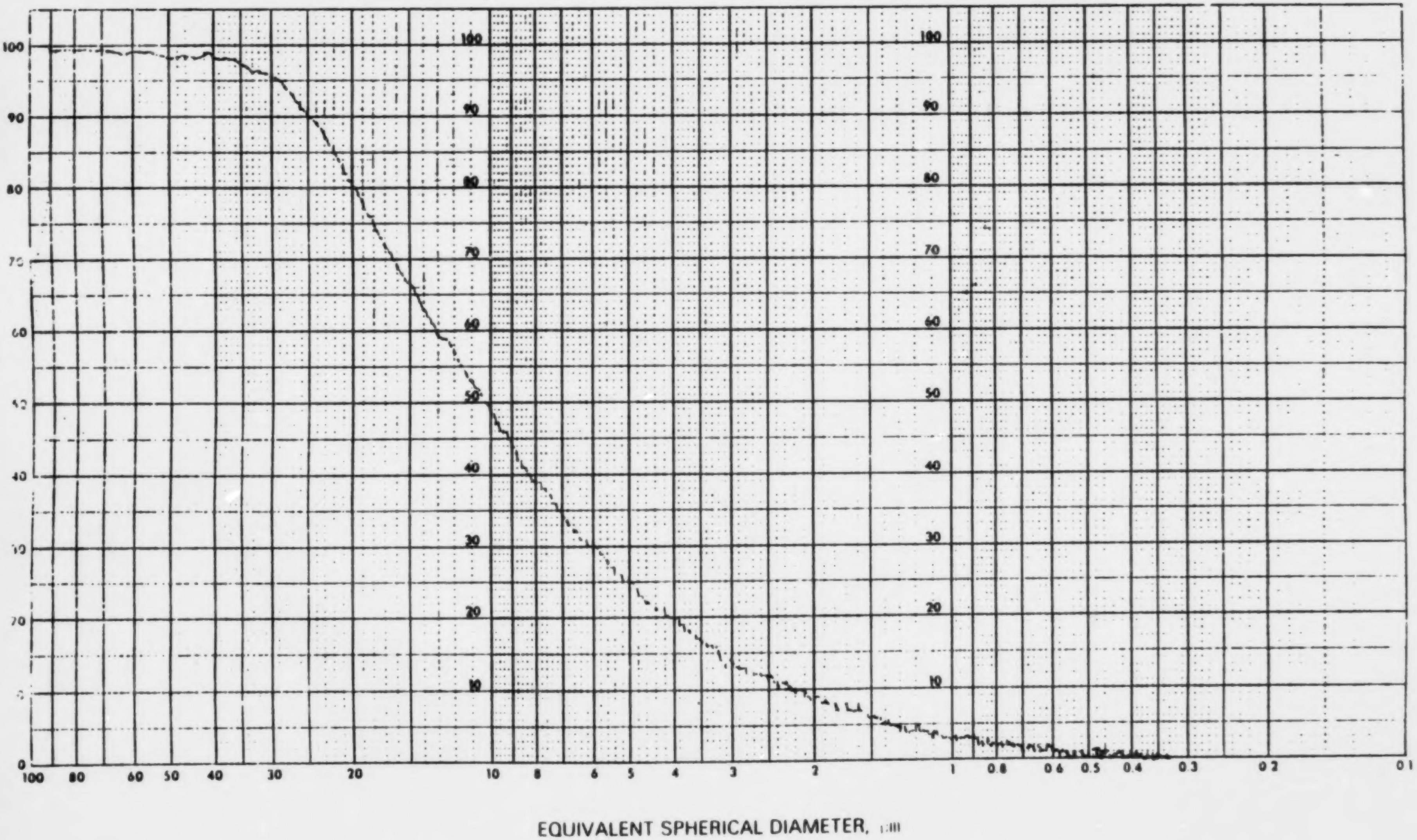
Organic grinding/silica/37.5% H_2O/blank/sedigraph analysis



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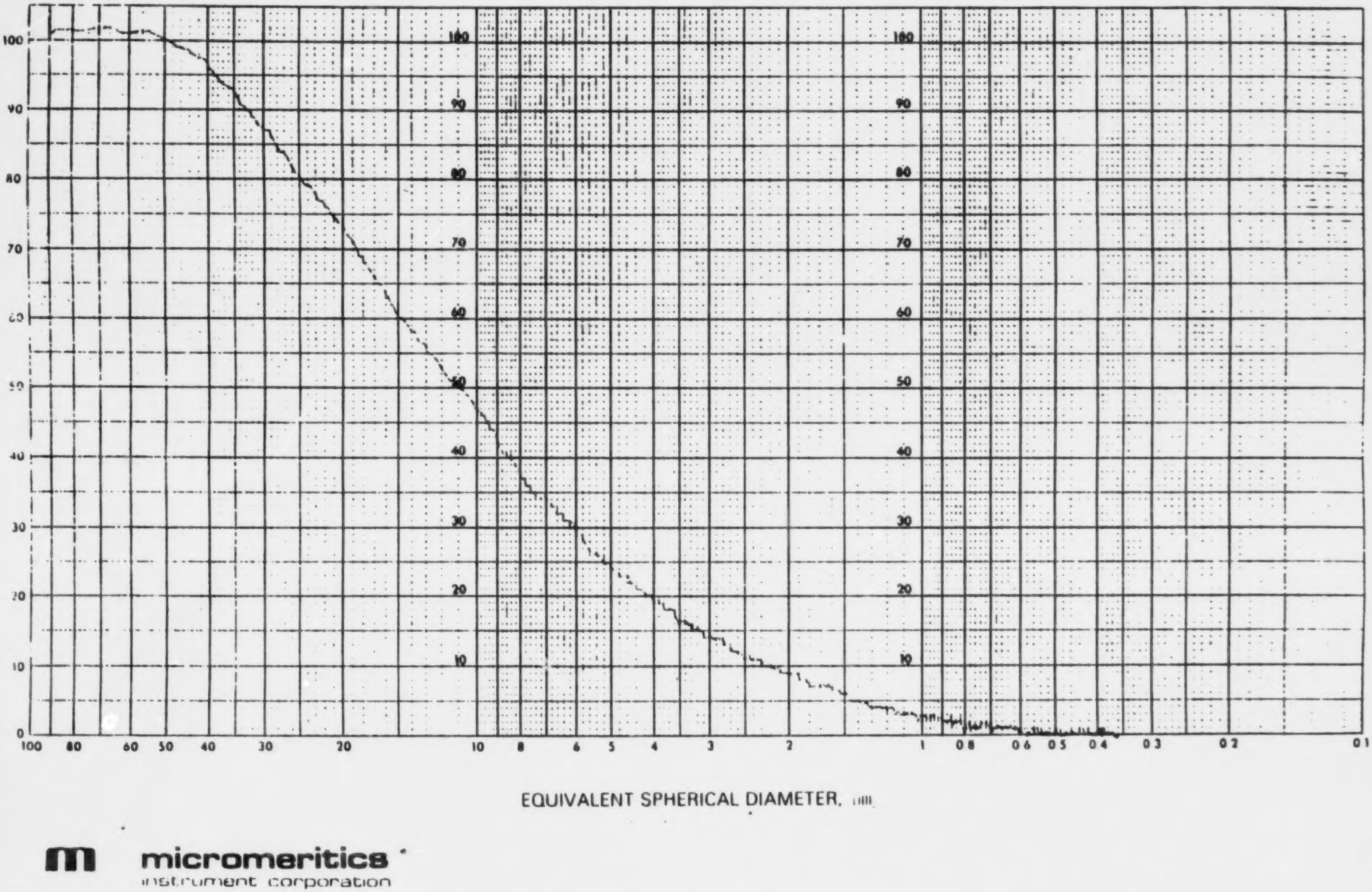
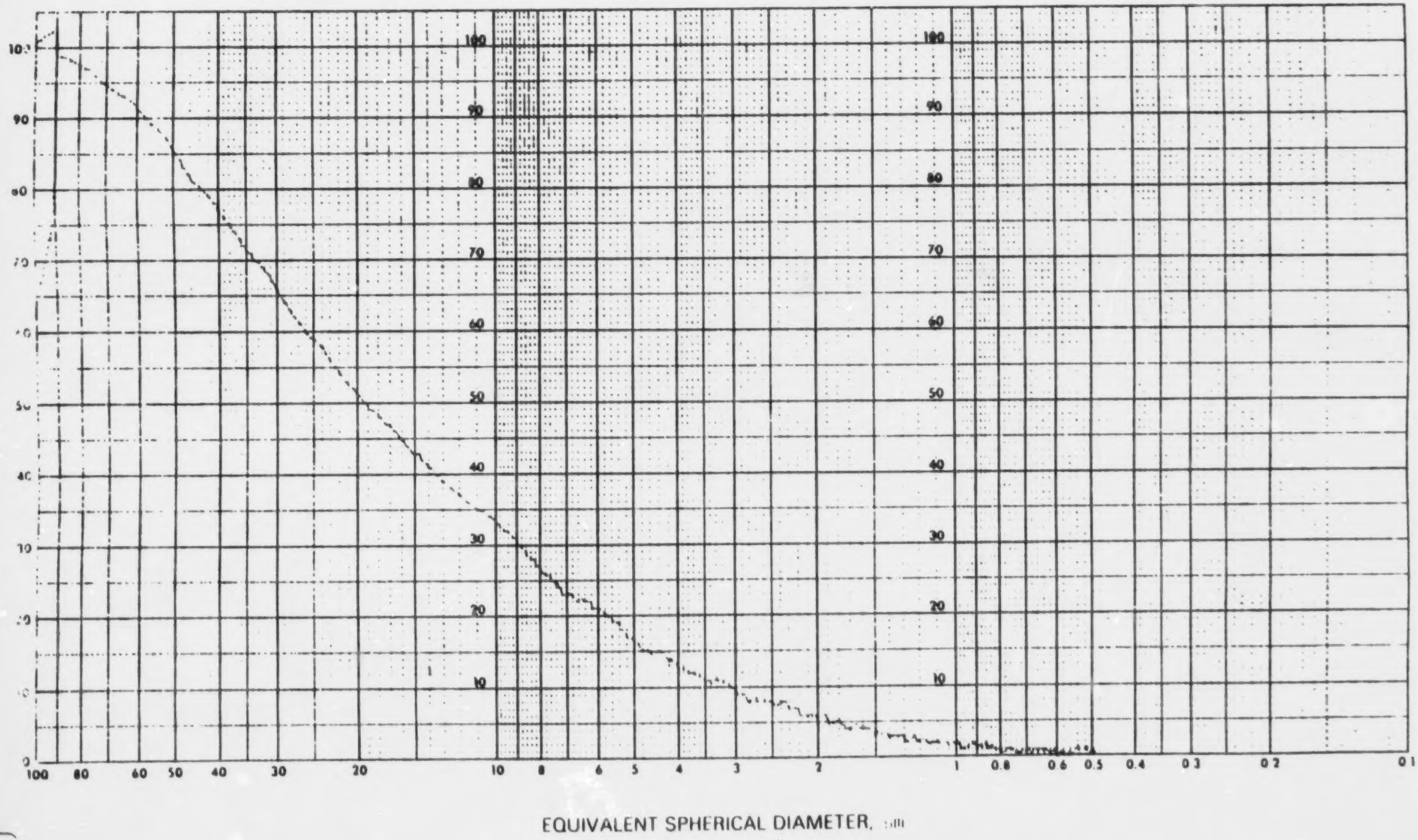
Organic grinding/silica/0.0% H_2O/propanol (3 g/kg)/sedigraph analysis



Organic grinding/silica/10% H_2O/propanol (3 g/kg)/sedigraph analysis



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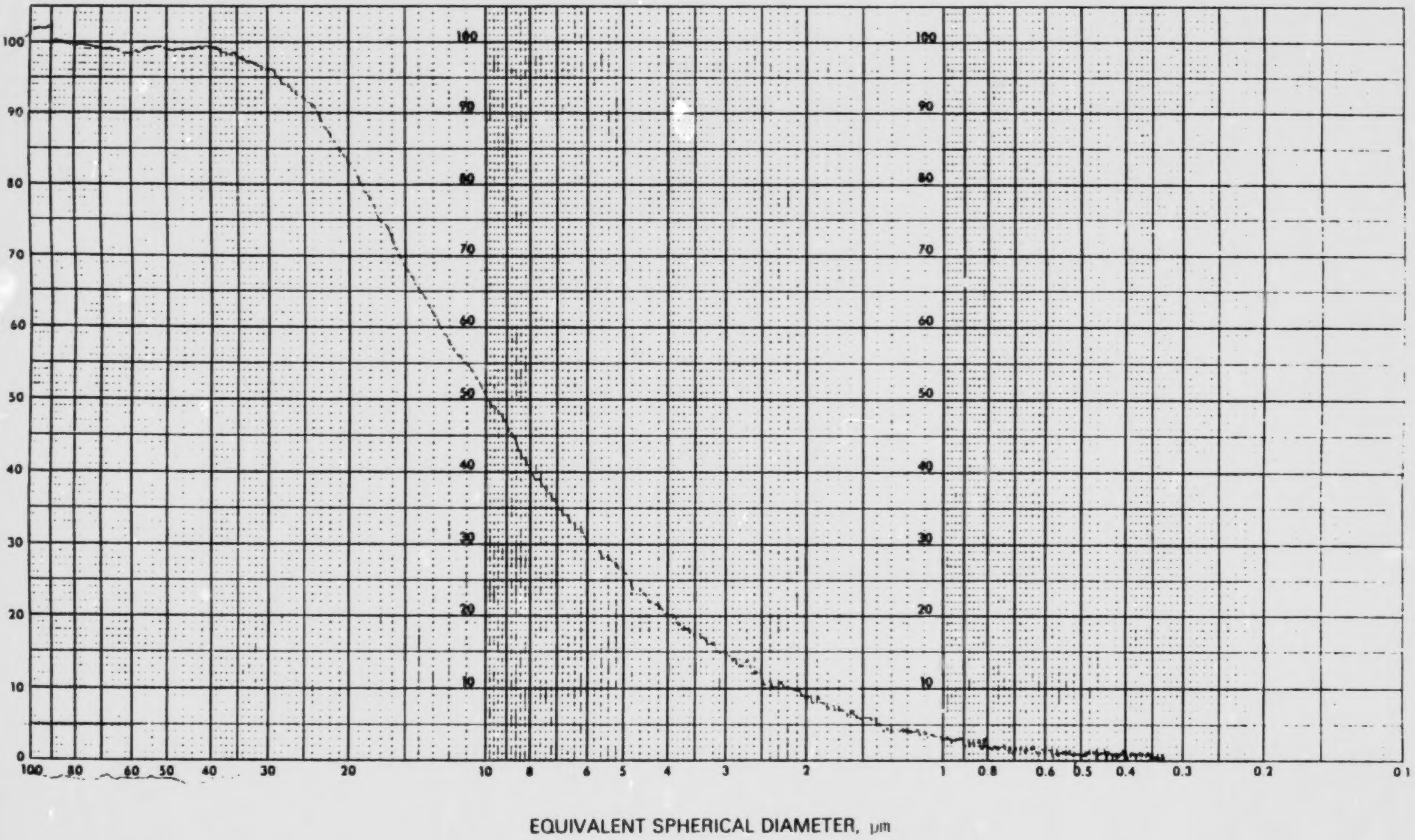
Organic grinding/silica/25% H_2O/propanol (3 g/kg)/sedigraph analysis



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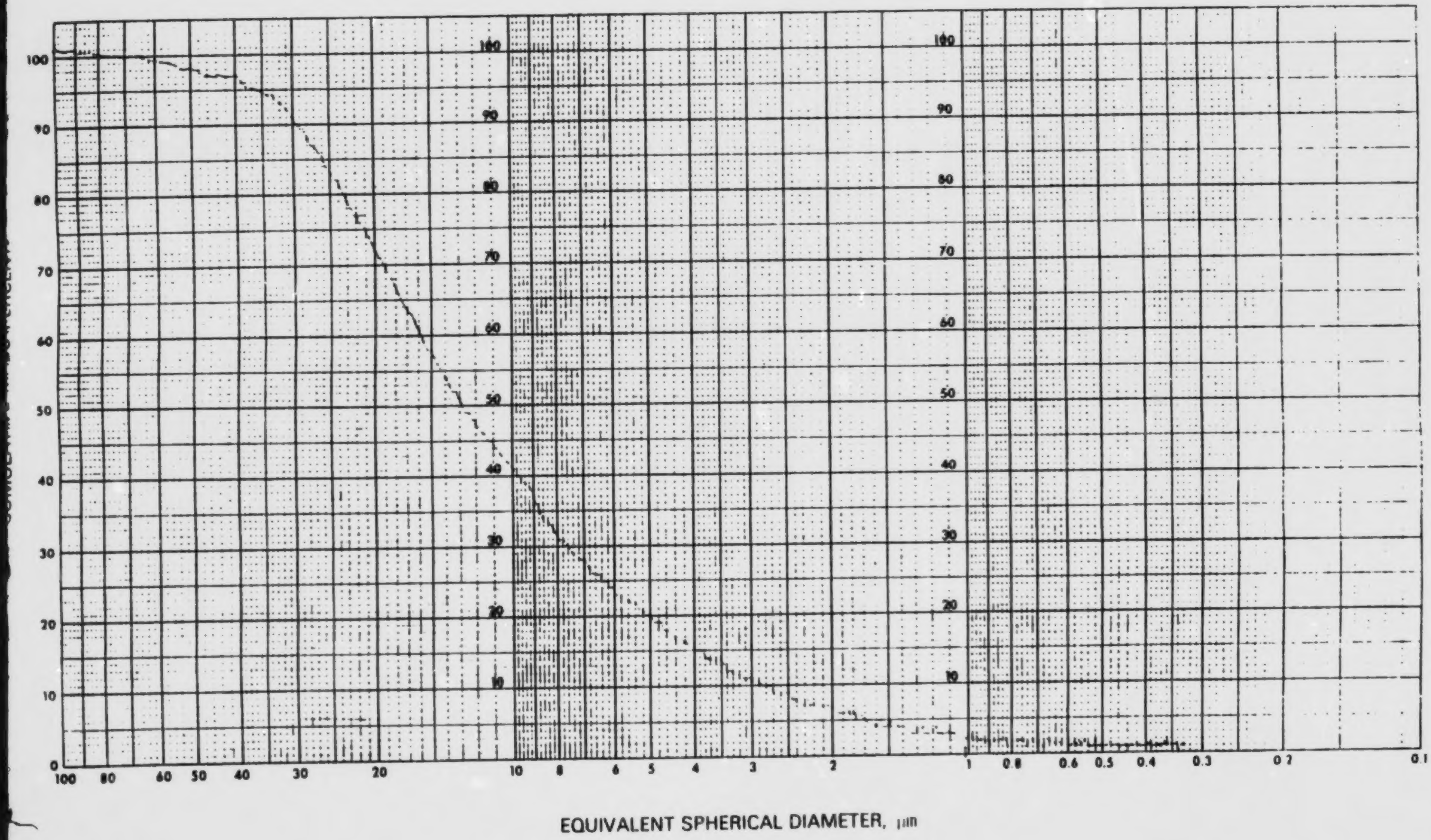
Organic grinding/silica/37.5% H_2O/propanol (3 g/kg)/sedigraph analysis



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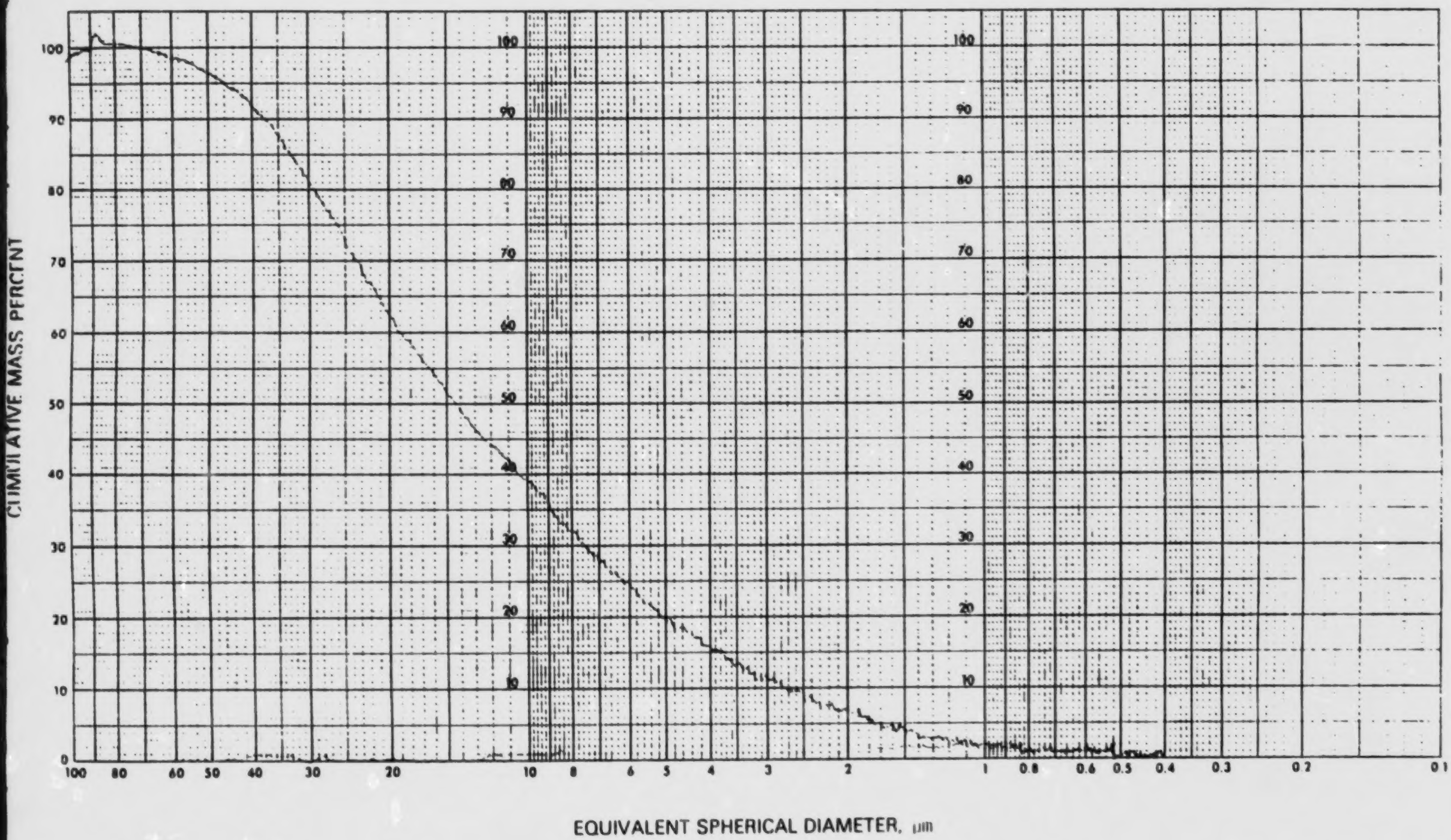
Organic grinding/silica/0.0% H_2O/propionic acid (3g k/g)/sedigraph analysis



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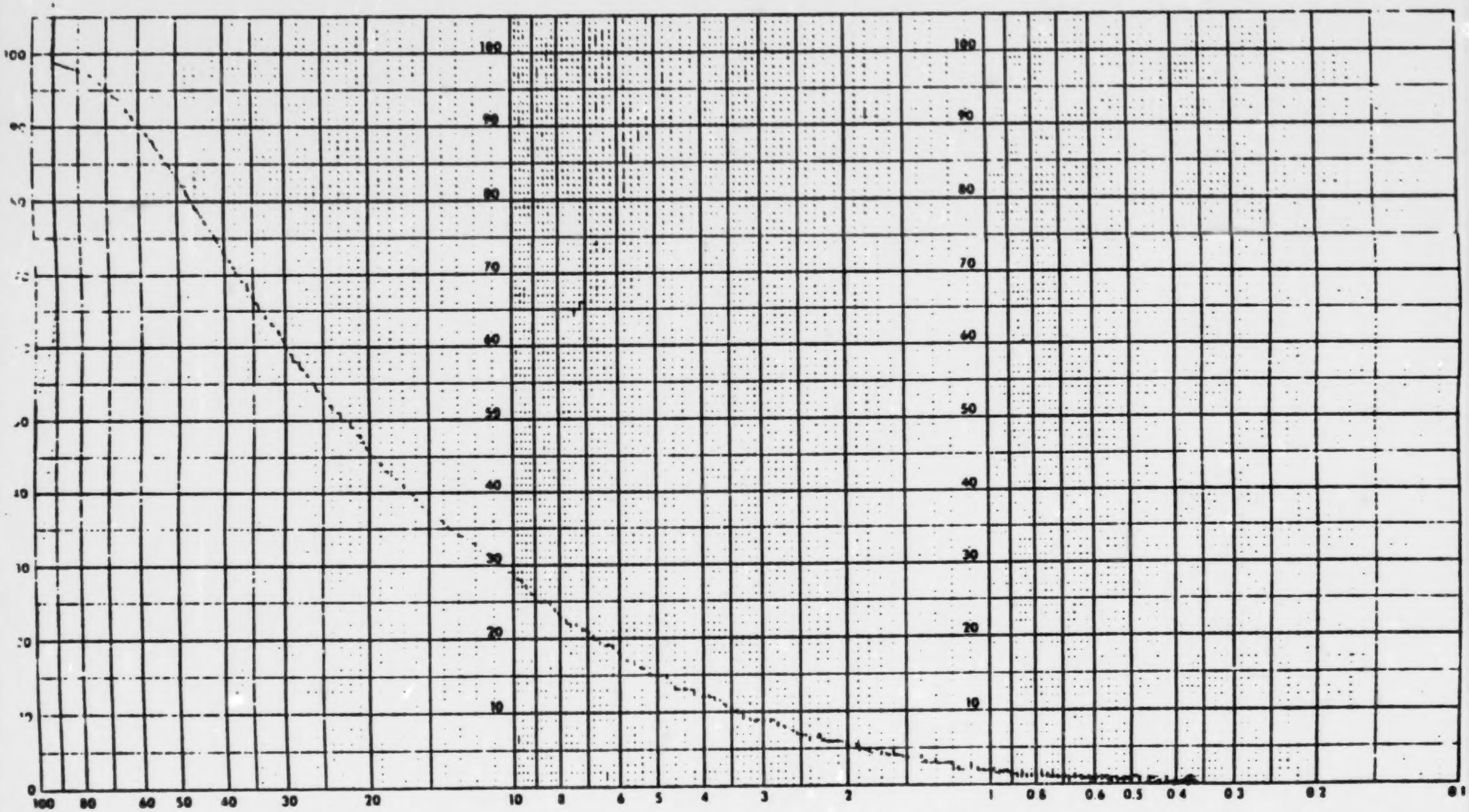
Organic grinding/silica/10% H_2O/propionic acid (3 g/kg)/sedigraph analysis



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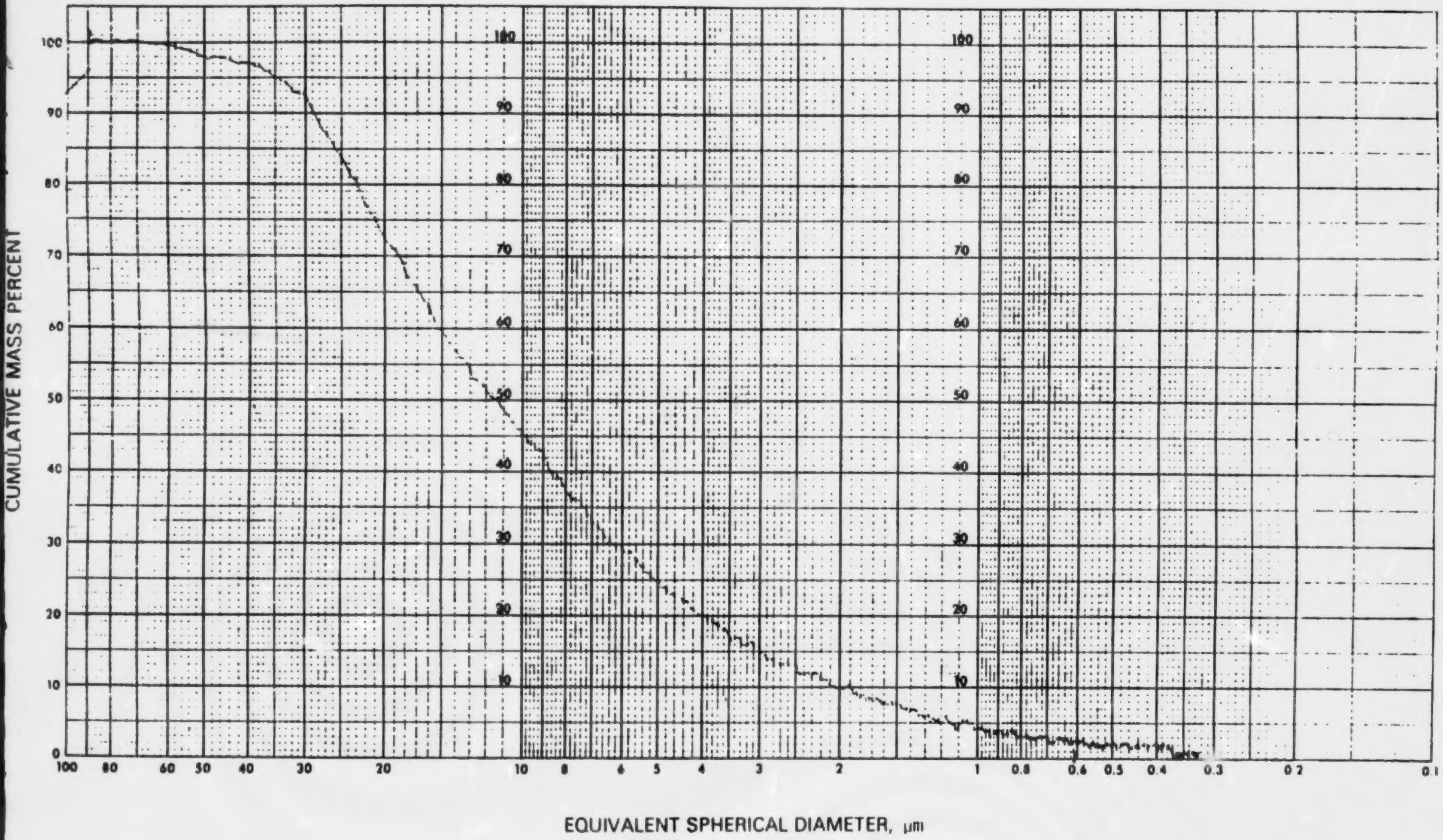
Organic grinding/silica/25% H_2O/propionic acid (3 g/kg)/sedigraph analysis



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APPENDIX C

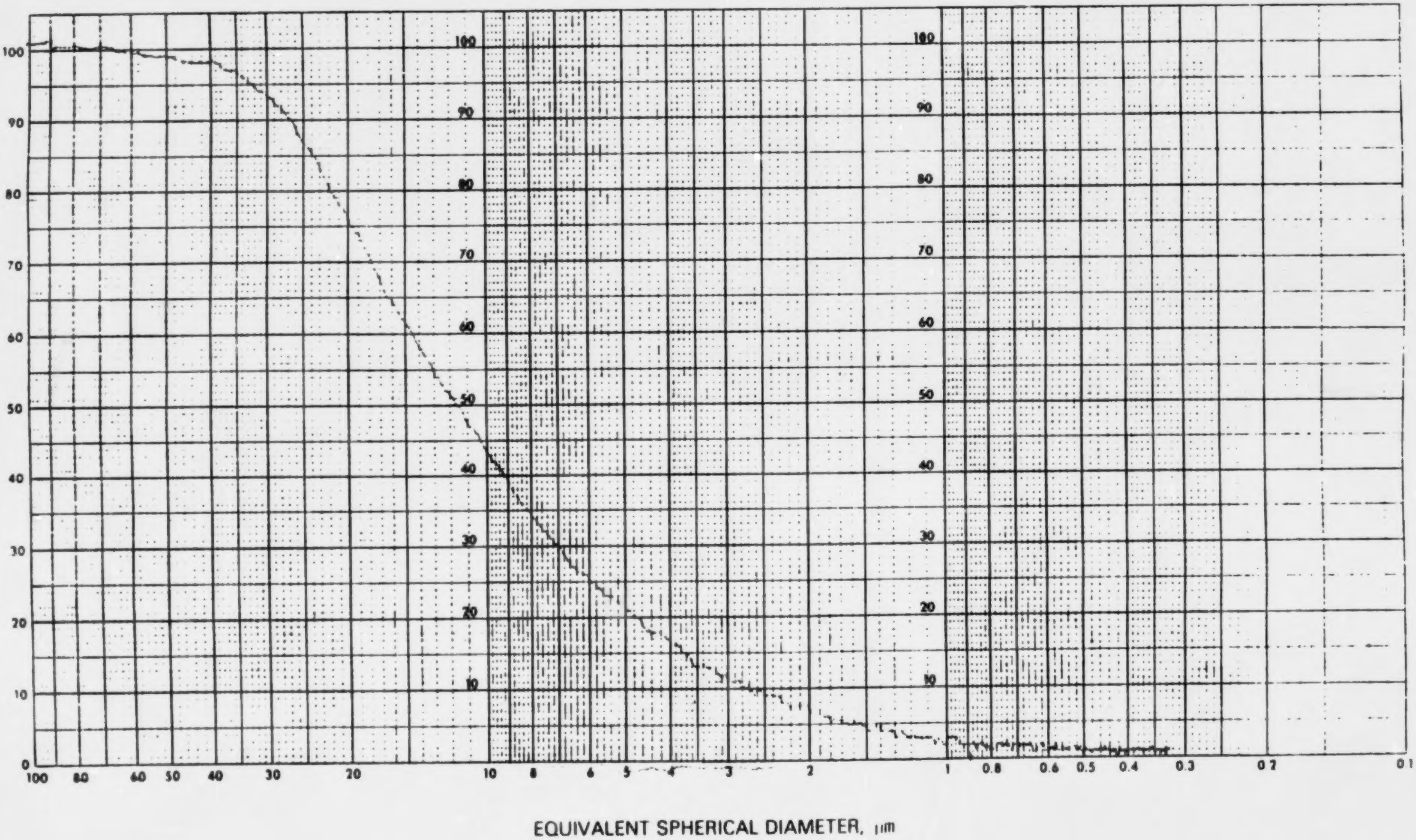
TALC GRINDING

Unground Talc

Moisture content = 0.16%, BET-surface area 1.782 m^2/g

% Particle Passing	Particle Size
95	56 um
80	35 um
50	18 um
20	10 um

Organic grinding/silica/37.5% H_2O/propionic acid (3 g/kg)/sedigraph analysis



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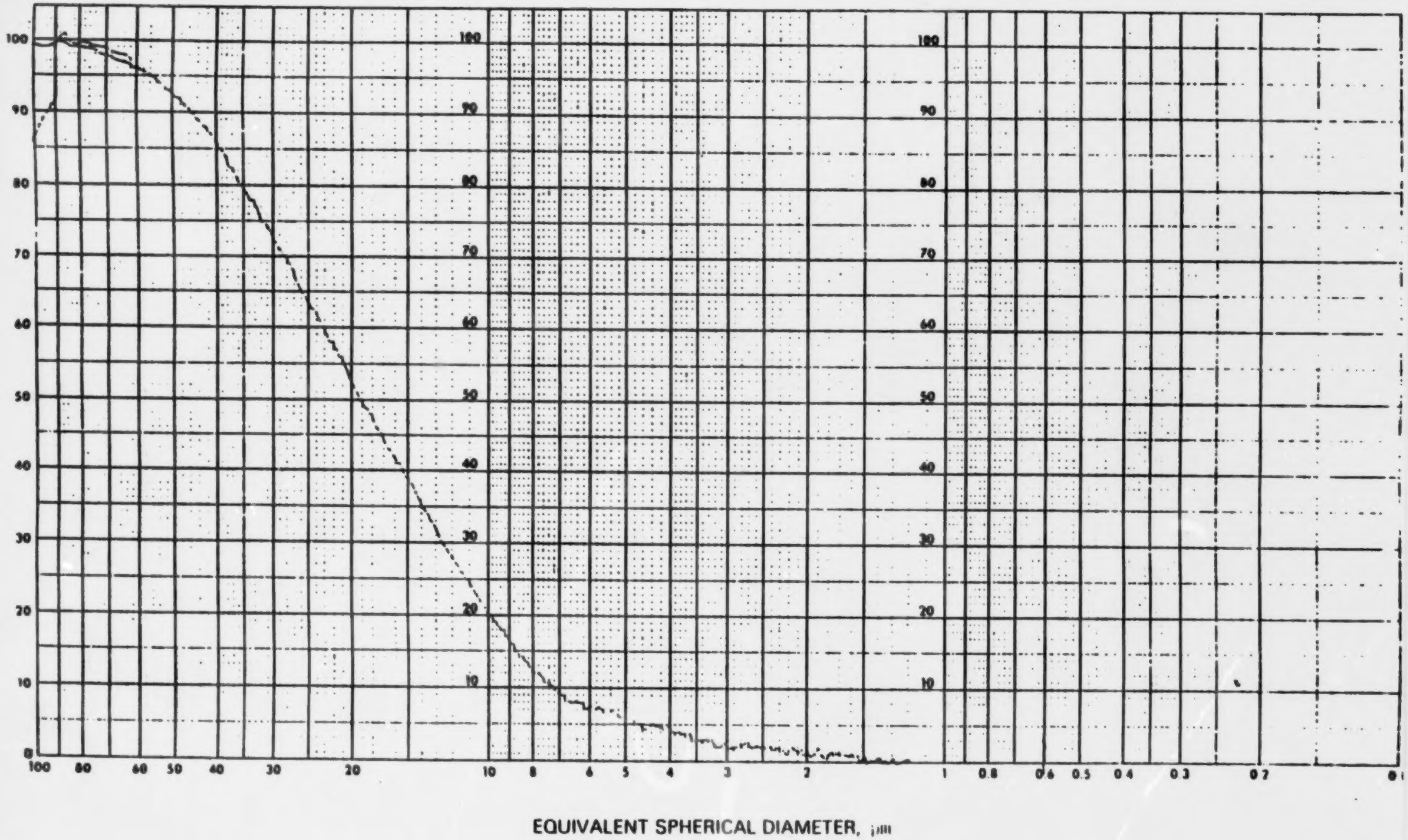
Head sample/talc/sedigraph analysis



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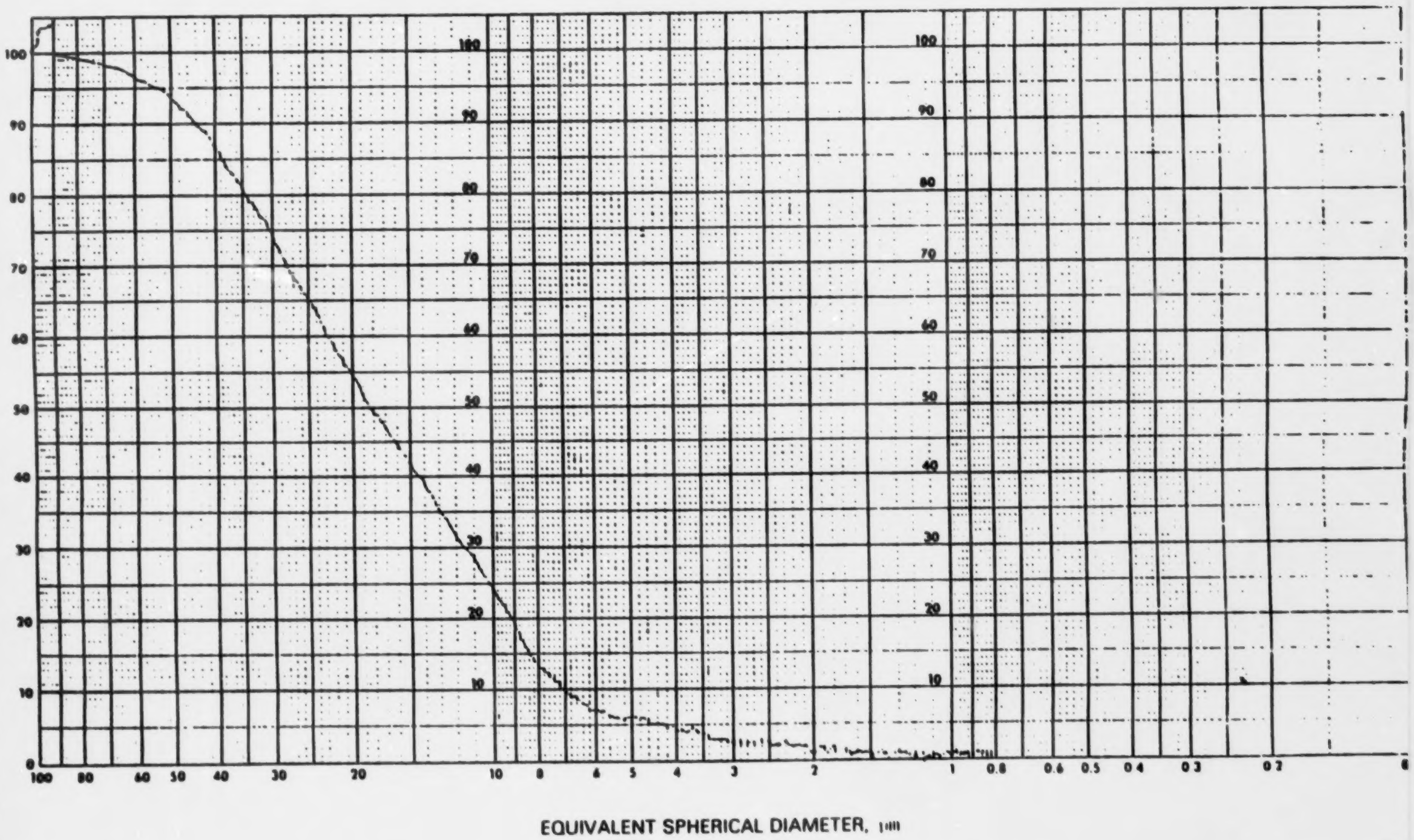
instrument corporation

Calibration grinding/talc/1.5 Kg/ 1/4 h/sedigraph analysis



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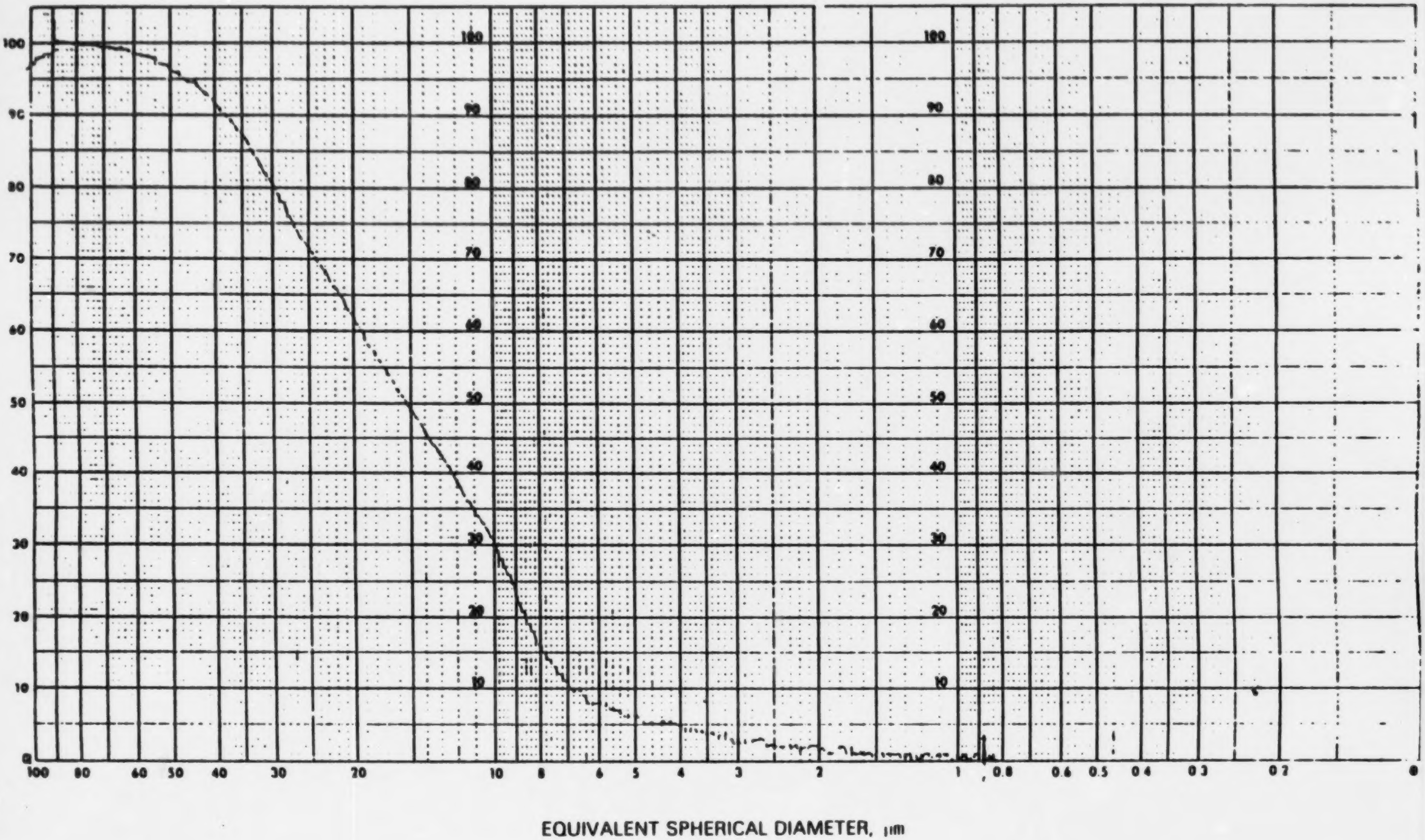
Calibration grinding/talc/1.5 Kg/ 1/2 h/sedigraph analysis



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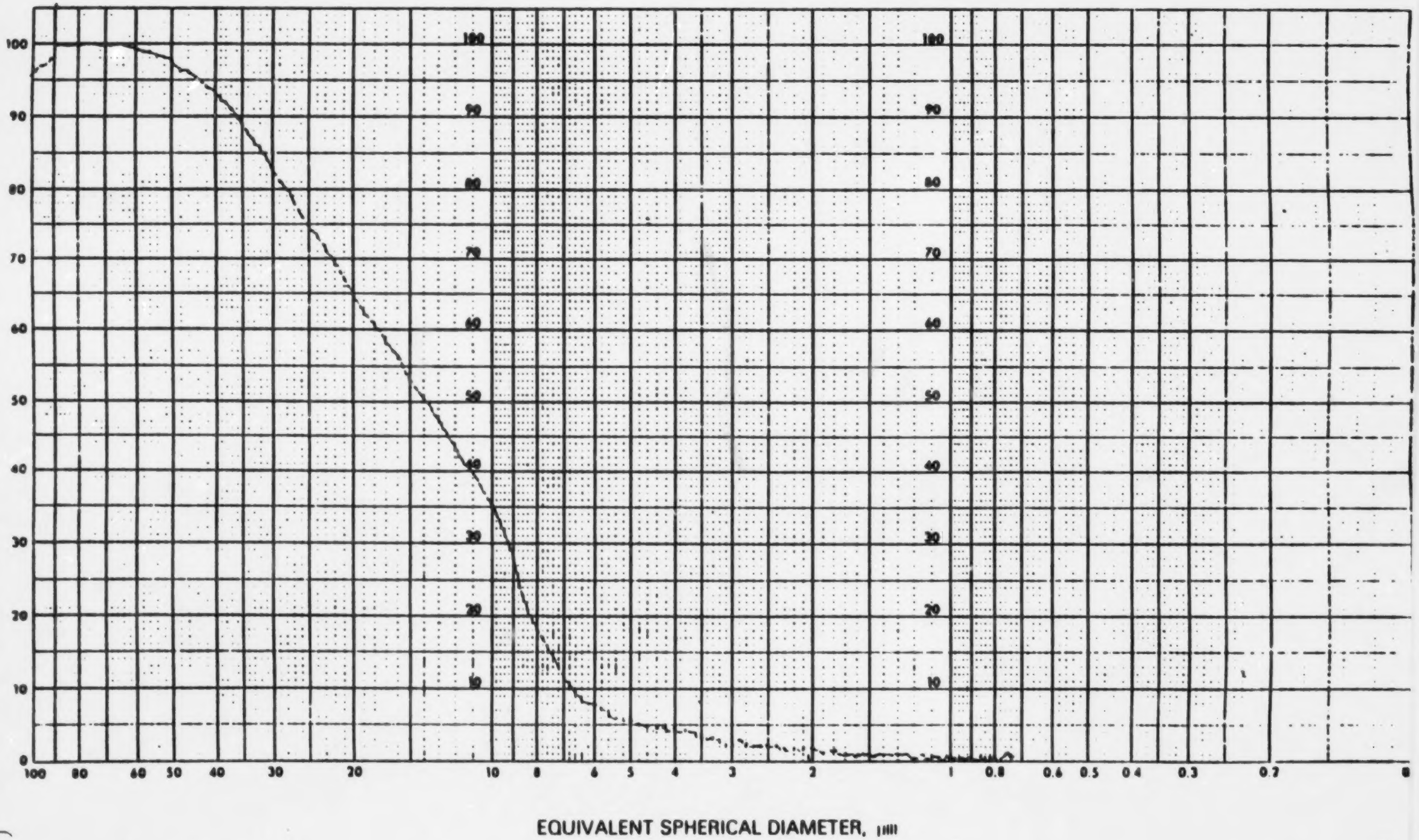
Calibration grinding/talc/1.5 Kg/1 h/sedigraph analysis



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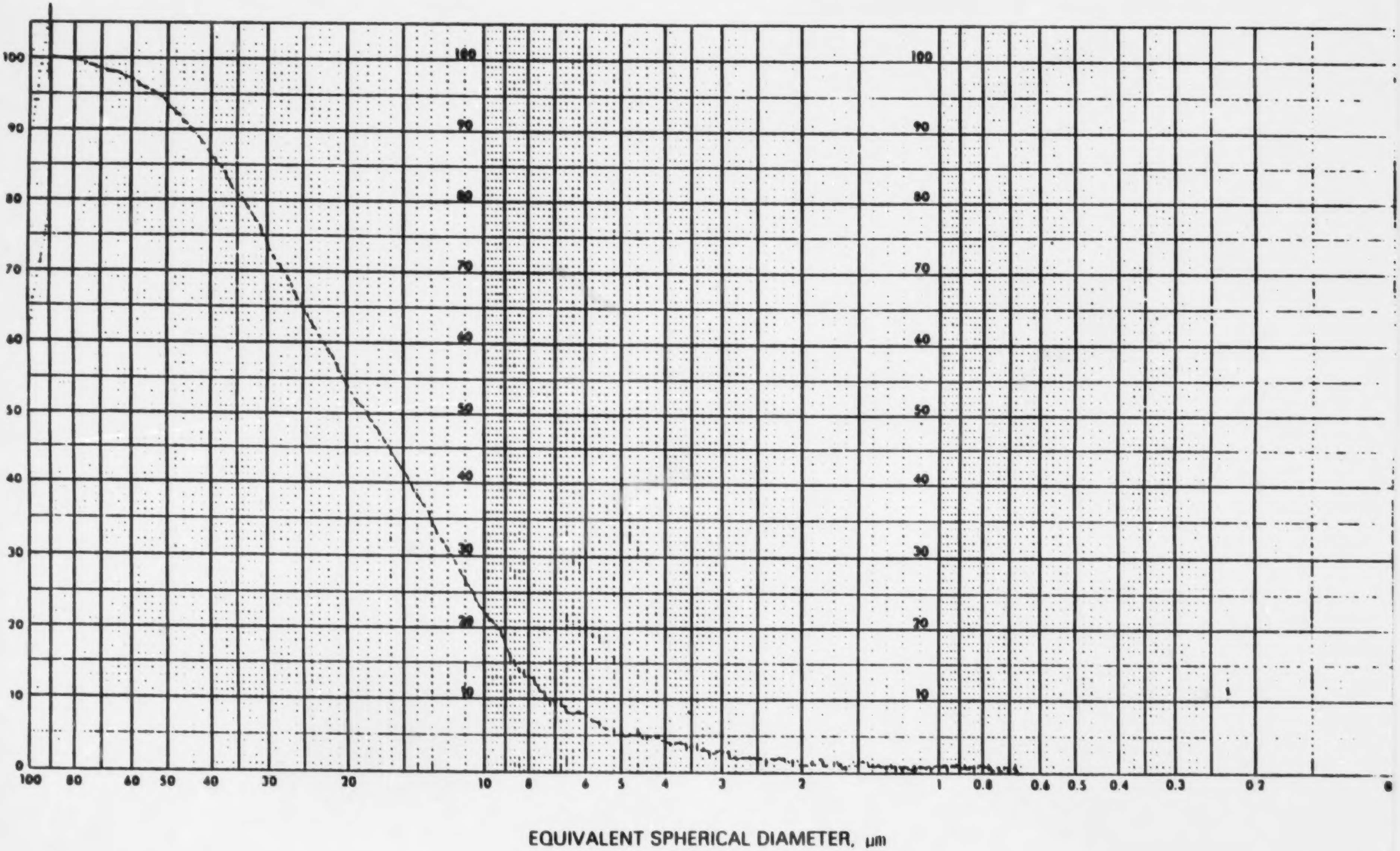
Calibration grinding/talc/1.0 Kg/ 1/4 h/sedigraph analysis



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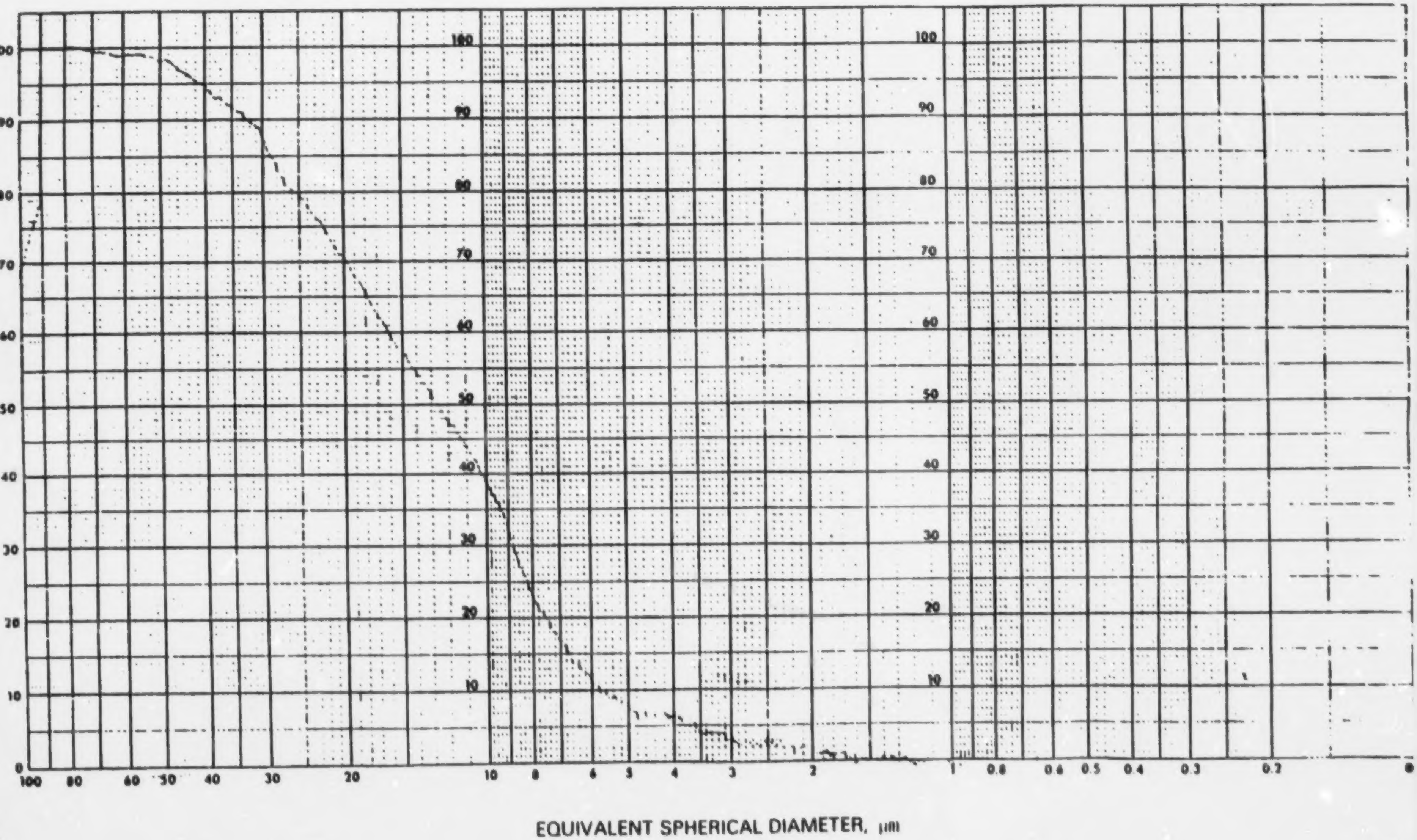
Calibration grinding/talc/1.0 Kg/ 1/2 h/sedigraph analysis



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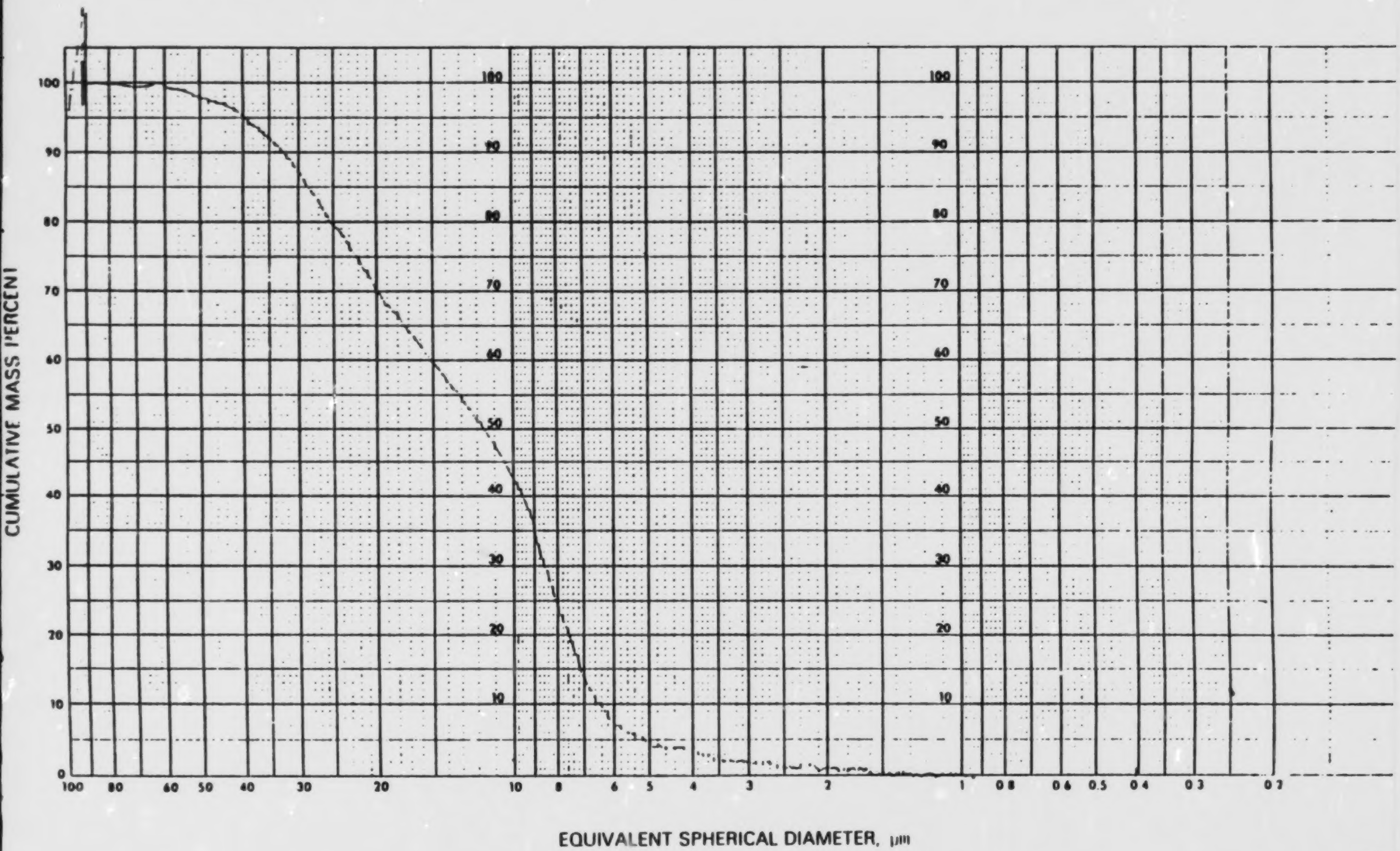
Calibration grinding/talc/1.0 Kg/1 h/sedigraph analysis



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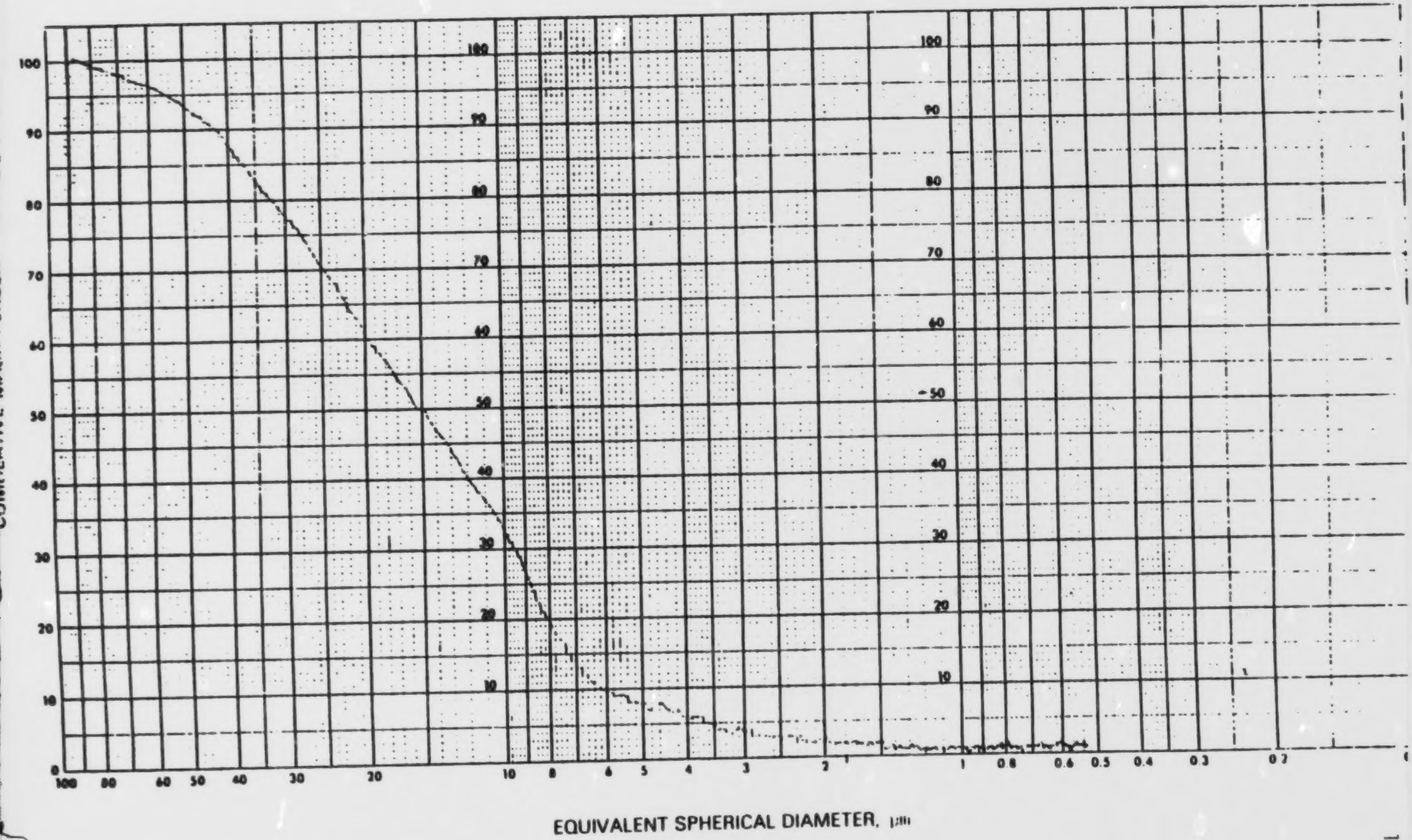
Calibration grinding/talc/0.5 Kg/ 1/4 h/sedigraph analysis



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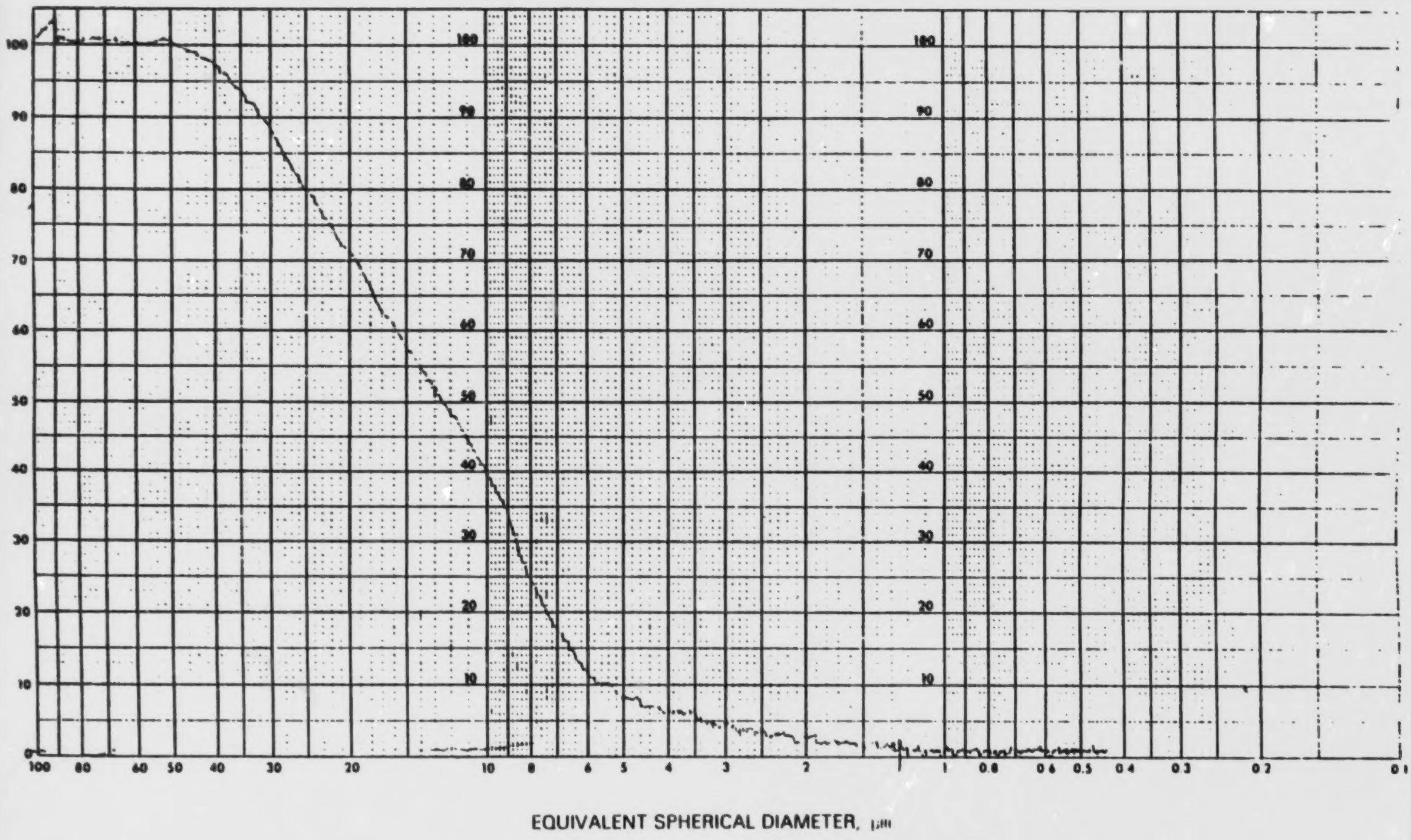
Calibration grinding/talc/0.5 Kg/ 1/2 h/sedigraph analysis



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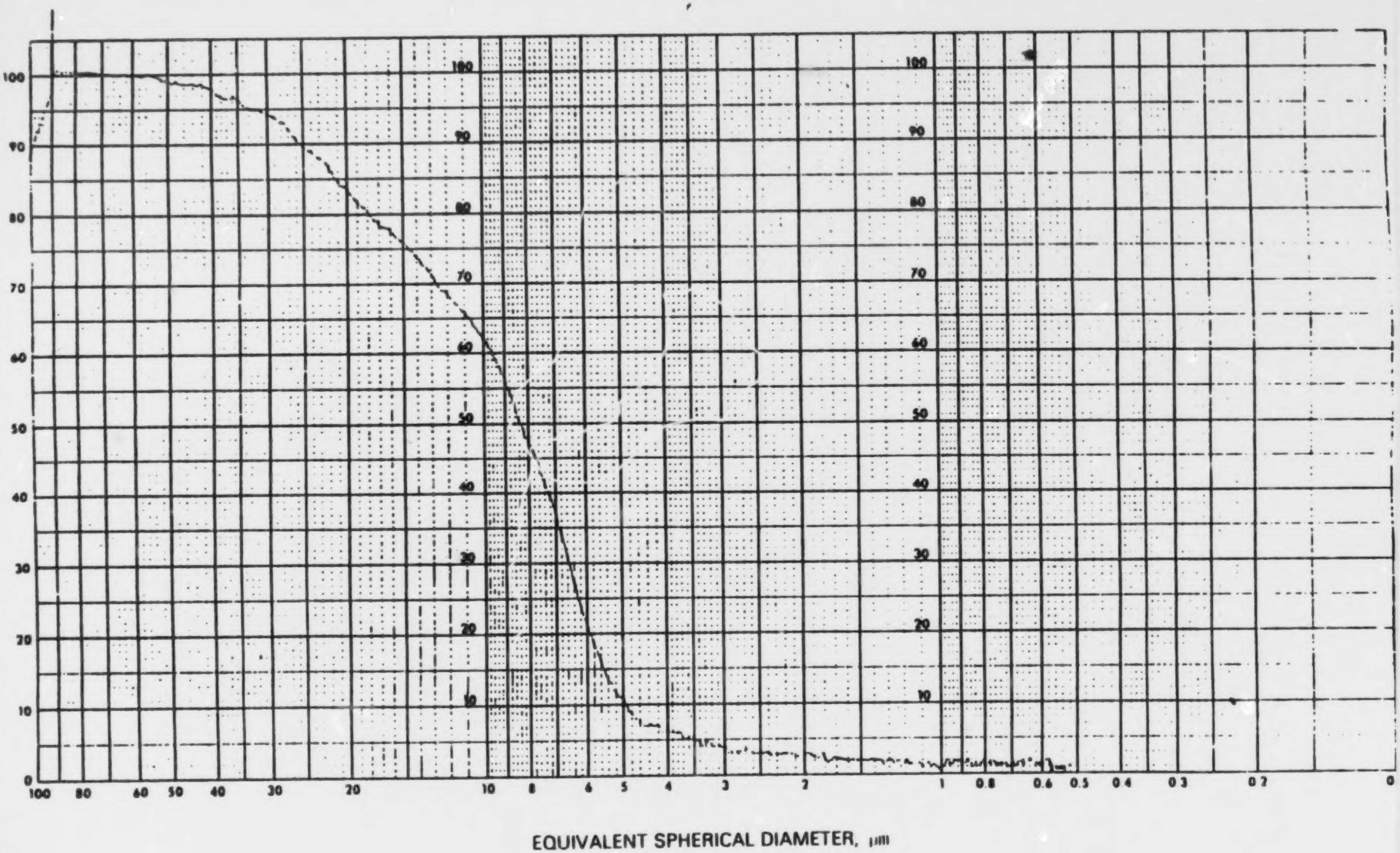
Calibration grinding/talc/0.5 Kg/1 h/sedigraph analysis



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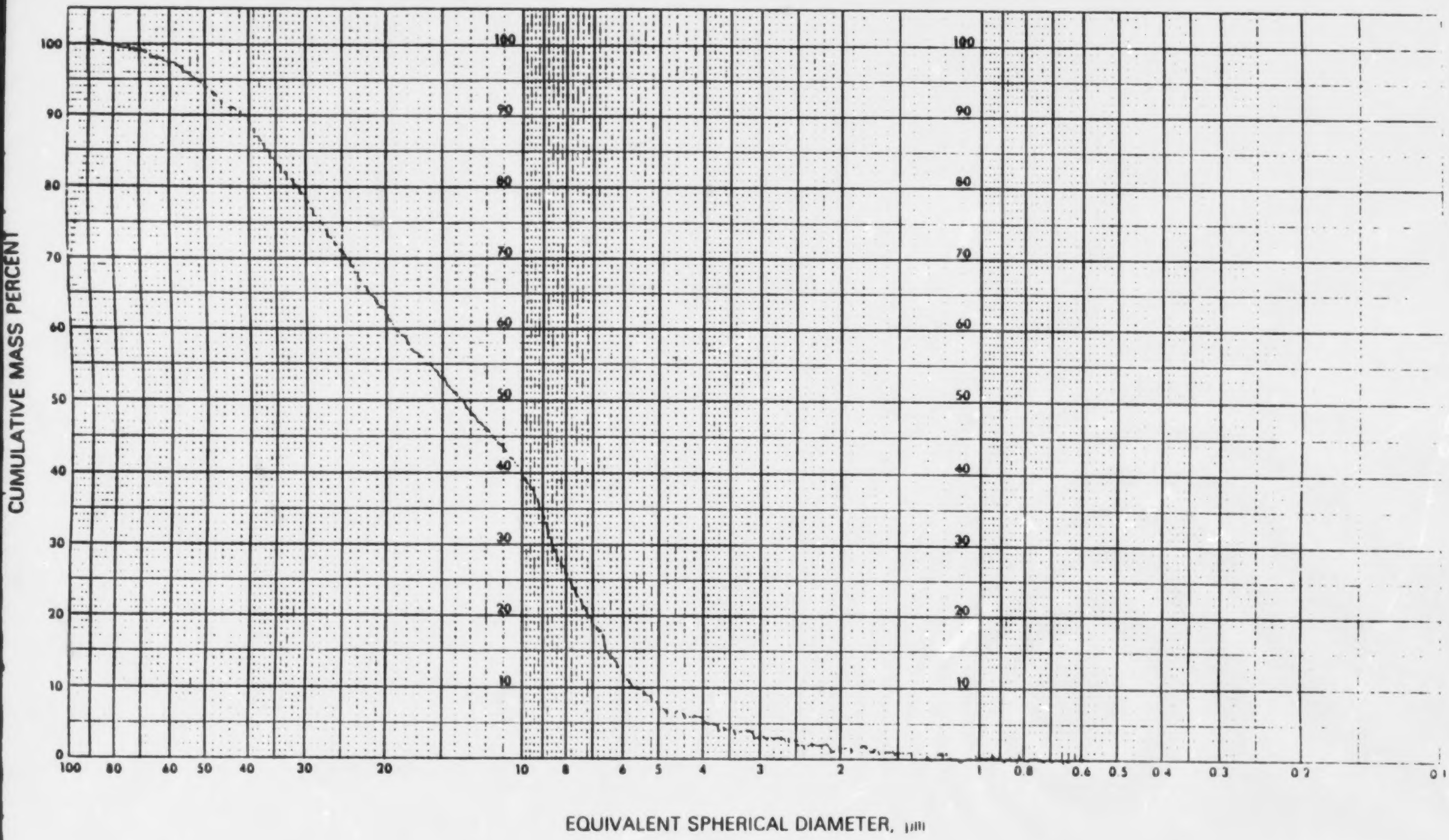
Organic grinding/talc/75 min/0.5 kg/blank/sedigraph analysis



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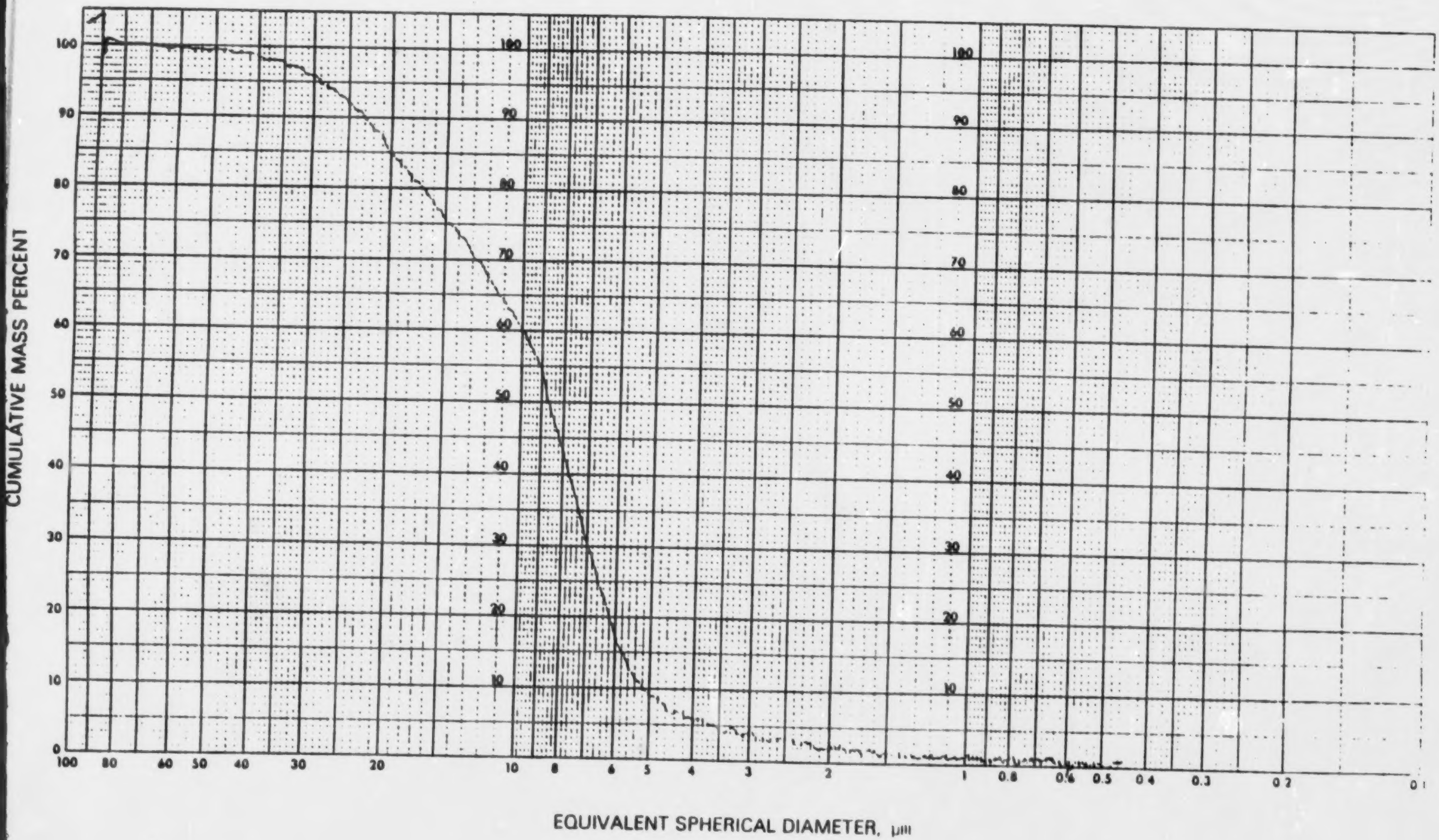
Organic grinding/talc/0.5 kg/propionic acid (3 g/kg)/sedigraph analysis



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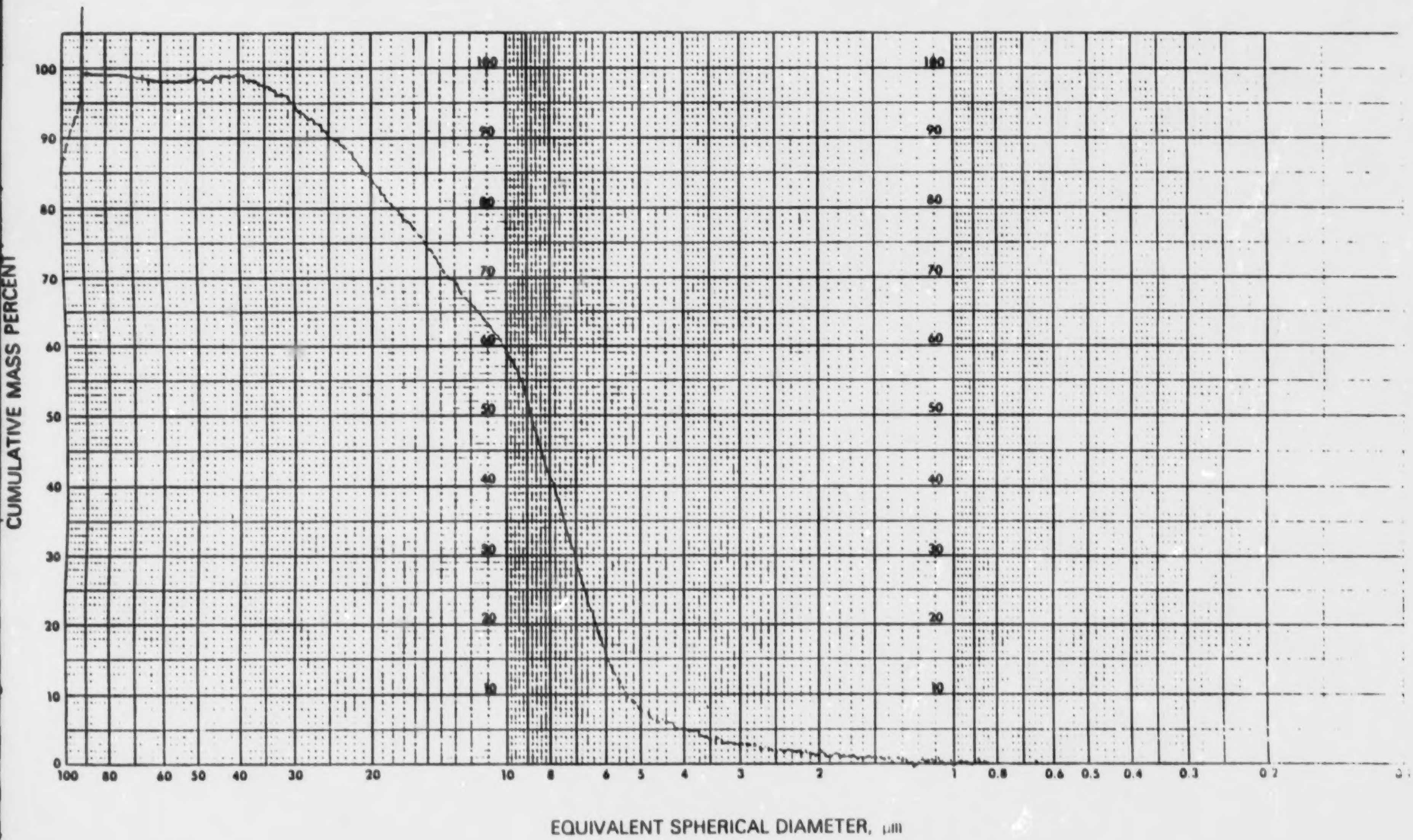
Organic grinding/talc/0.5 kg/propanol (3 g/kg)/sedigraph analysis



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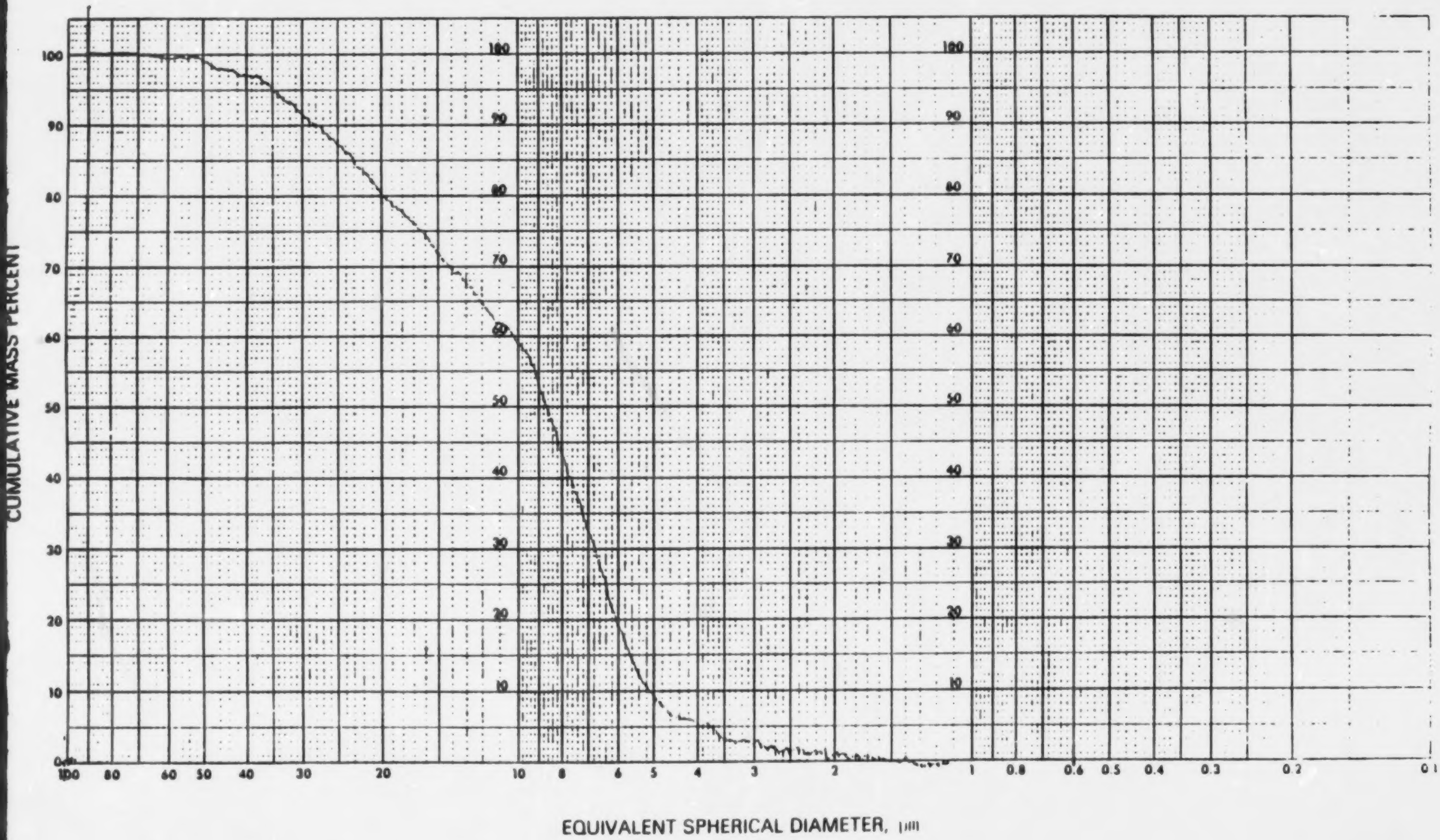
Organic grinding/talc/0.5 kg/ether (3 g/kg)/sedigraph analysis



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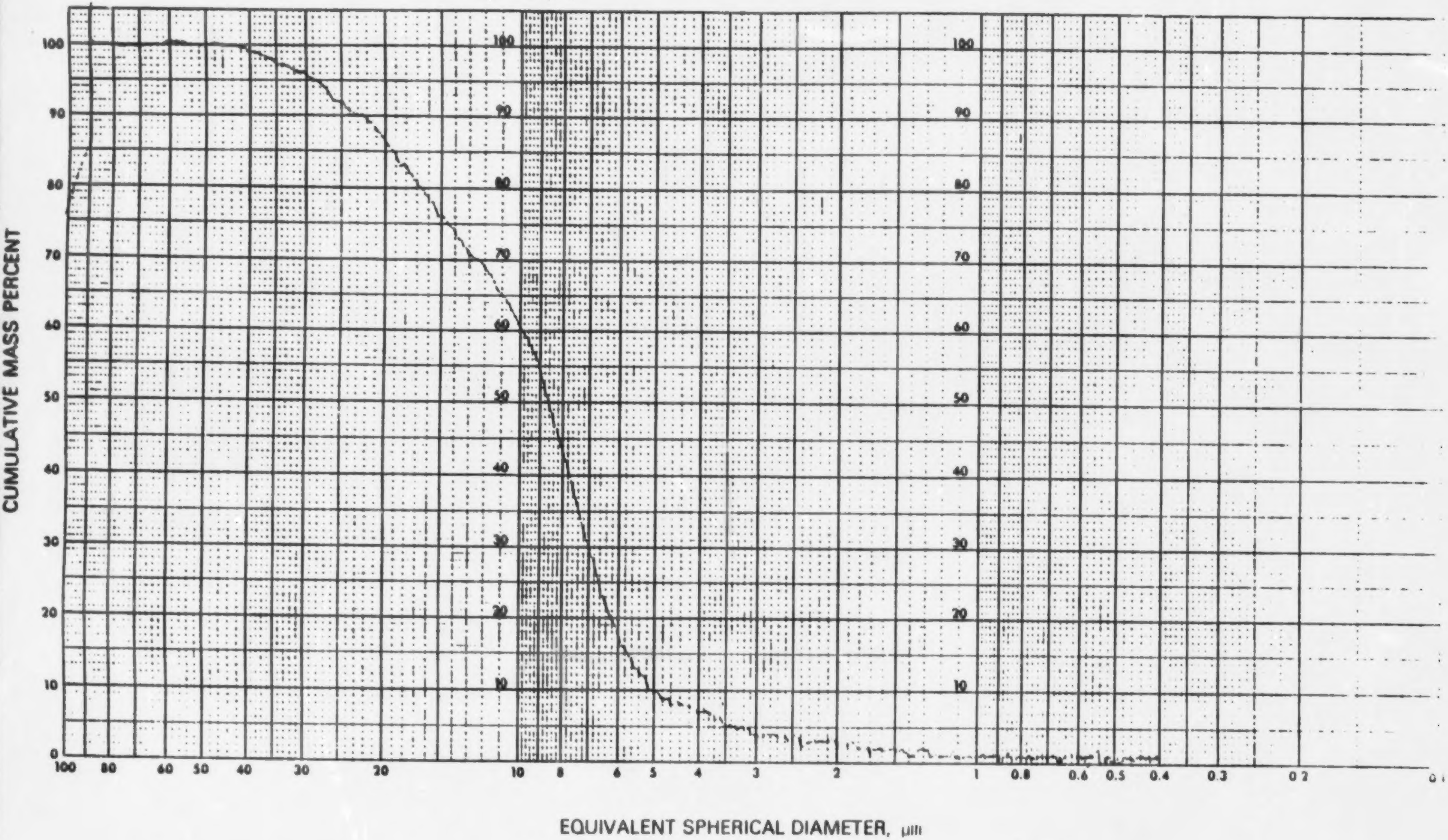
Organic grinding/talc/75 min/0.5 kg/ketone (3 g/kg)/sedigraph analysis



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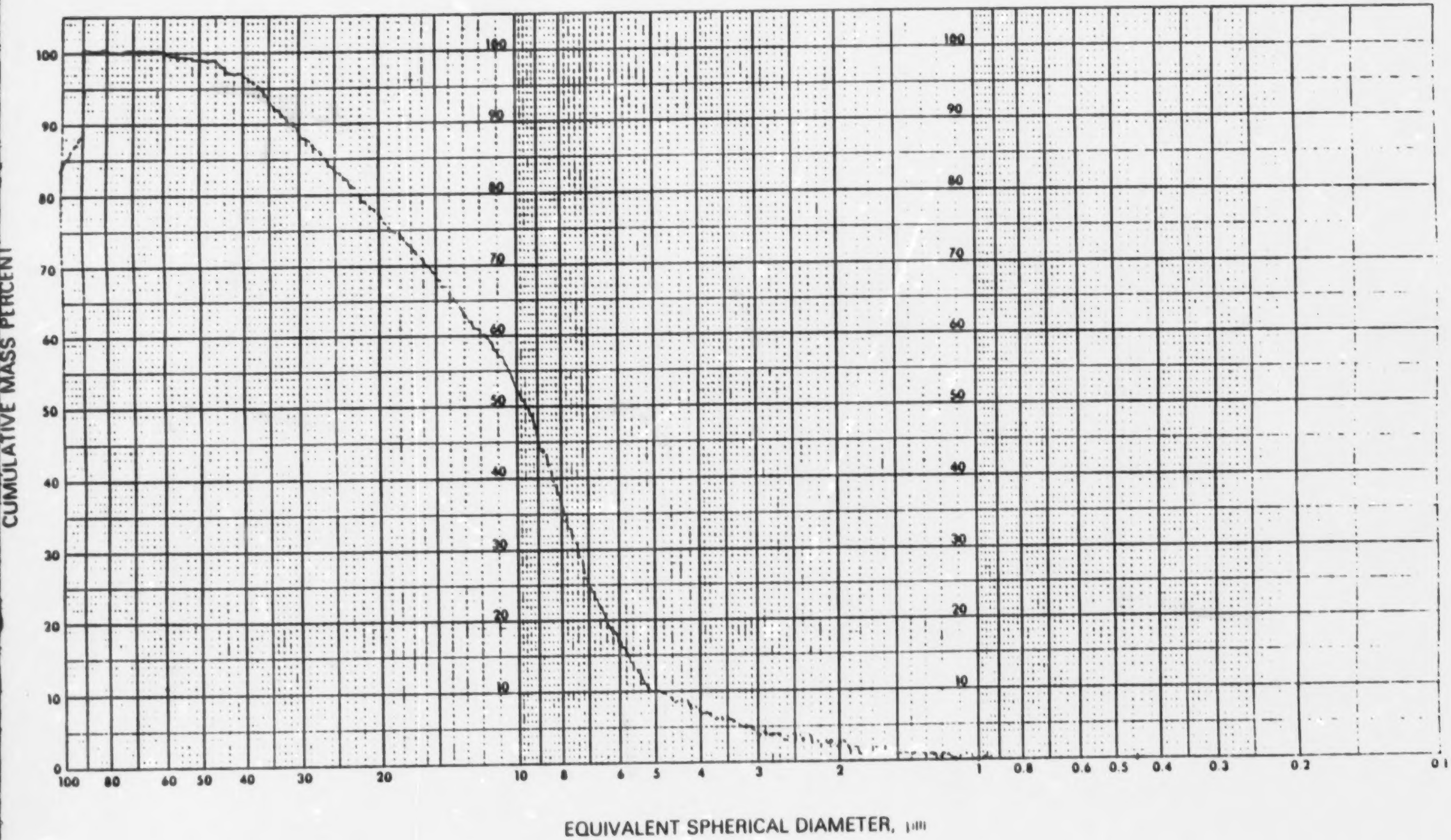
Organic grinding/talc/75 min/0.5 kg/kerosene (3 g/kg)/sedigraph analysis



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APPENDIX D

CALCITE GRINDING

SCREEN ANALYSIS OF CALCITE HEAD SAMPLE

TIME 0 hr/100g

mesh	total grams left on screen	% Passing
6 mesh	43.1 g	95.69 %
14 mesh	90.59 g	5.1 %
20 mesh	2.6 g	2.5 %
28 mesh	0.31 g	2.19 %
35 mesh	0.05 g	2.14 %
65 mesh	0.03 g	2.11 %
pan	2.13 g	--

MILL CALIBRATION OF CALCITE

SCREEN ANALYSIS

TIME 1 hr/500g

mesh	total grams left on screen	% Passing
6 mesh	0.57 g	99.43 %
14 mesh	1.35 g	98.08 %
20 mesh	0.8 g	97.28 %
28 mesh	0.5 g	96.78 %
35 mesh	0.6 g	96.18 %
65 mesh	0.32 g	95.86 %
pan	95.86 g	--

MILL CALIBRATION OF CALCITE

SCREEN ANALYSIS

TIME 1 hr/1000g

mesh	total grams left on screen	% Passing
6 mesh	0.9 g	99.1 %
14 mesh	4.53 g	94.57 %
20 mesh	0.45 g	94.12 %
28 mesh	0.26 g	93.86 %
35 mesh	0.23 g	93.63 %
65 mesh	0.76 g	92.87 %
pan	92.87 g	--

MILL CALIBRATION OF CALCITE

SCREEN ANALYSIS

TIME 1 hr/1500g

mesh	total grams left on screen	% Passing
6 mesh	1.54 g	98.46 %
14 mesh	13.86 g	84.6 %
20 mesh	2.36 g	82.24 %
28 mesh	1.41 g	80.83 %
35 mesh	1.07 g	79.76 %
65 mesh	2.77 g	76.99 %
pan	76.99 g	--

MILL CALIBRATION OF CALCITE
SCREEN ANALYSIS

TIME 1/2 hr/500g

mesh	total grams left on screen	% Passing
6 mesh	2.24 g	97.76 %
14 mesh	15.54 g	82.22 %
20 mesh	1.47 g	80.75 %
28 mesh	0.81 g	79.94 %
35 mesh	0.63 g	79.31 %
65 mesh	1.40 g	77.91 %
pan	77.91 g	--

MILL CALIBRATION OF CALCITE

SCREEN ANALYSIS

TIME 1/2 hr/1000g

mesh	total grams left on screen	% Passing
6 mesh	2.56 g	97.44 %
14 mesh	24.75 g	72.69 %
20 mesh	3.98 g	68.71 %
28 mesh	2.40 g	66.31 %
35 mesh	1.80 g	64.51 %
65 mesh	3.83 g	60.68 %
pan	60.68 g	--

MILL CALIBRATION OF CALCITE

SCREEN ANALYSIS

TIME 1/2 hr/1500g

mesh	total grams left on screen	% Passing
6 mesh	2.53 g	97.47 %
14 mesh	31.0 g	66.47 %
20 mesh	6.2 g	60.27 %
28 mesh	3.7 g	56.57 %
35 mesh	2.7 g	53.87 %
65 mesh	5.55 g	48.32 %
pan	48.32 g	--

MILL CALIBRATION OF CALCITE
SCREEN ANALYSIS

TIME 15 min/500g

mesh	total grams left on screen	% Passing
6 mesh	4.00 g	96. %
14 mesh	29.30 g	66.7 %
20 mesh	3.73 g	62.97 %
28 mesh	2.30 g	60.67 %
35 mesh	1.63 g	59.04 %
65 mesh	3.50 g	55.54 %
pan	55.54 g	--

MILL CALIBRATION OF CALCITE

SCREEN ANALYSIS

TIME 15 min/1000g

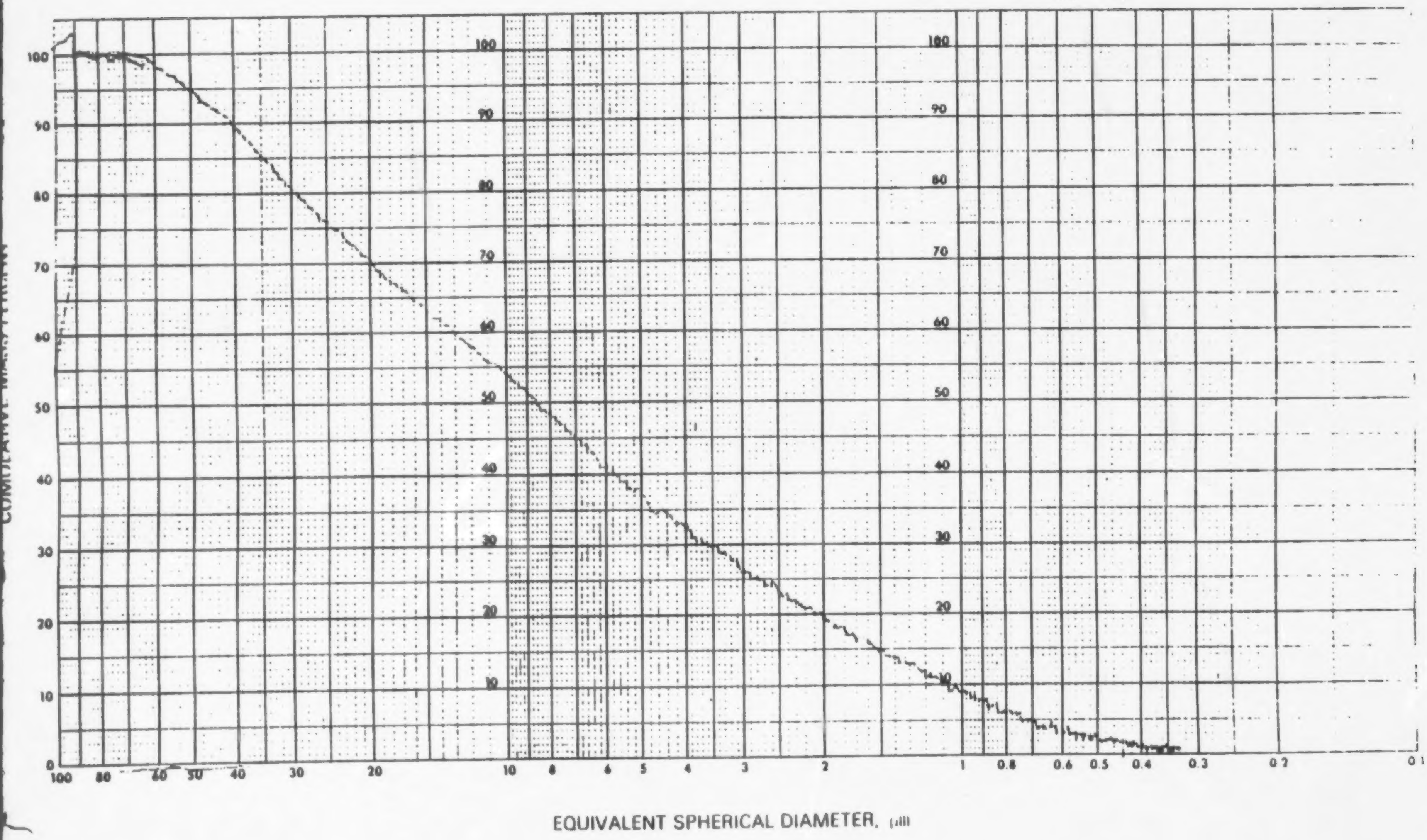
mesh	total grams left on screen	% Passing
6 mesh	2.30 g	97.7 %
14 mesh	35.53 g	62.17 %
20 mesh	7.14 g	55.03 %
28 mesh	4.44 g	50.59 %
35 mesh	3.33 g	47.26 %
65 mesh	6.43 g	40.83 %
pan	40.83 g	--

MILL CALIBRATION OF CALCITE
SCREEN ANALYSIS

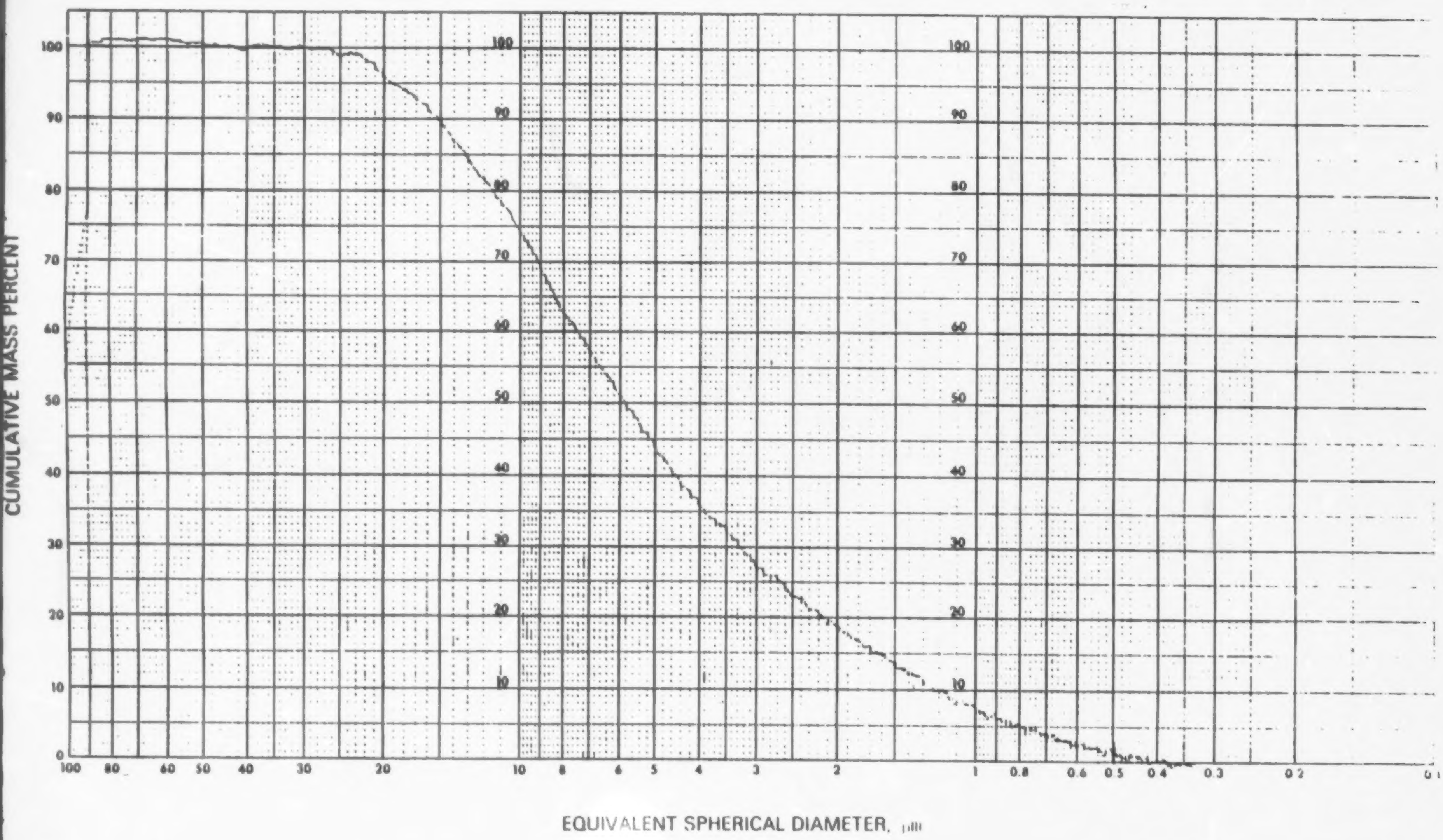
TIME 15 min/1500g

mesh	total grams left on screen	% Passing
6 mesh	1.08 g	98.92 %
14 mesh	46.87 g	52.05 %
20 mesh	8.84 g	43.21 %
28 mesh	5.41 g	37.80 %
35 mesh	3.9 g	33.96 %
65 mesh	6.55 g	27.35 %
pan	27.35 g	--

Organic grinding of calcite/70 min/0.5 kg/-150 um/blank/sedigraph analysis



Organic grinding of calcite/70 min/0.5 kg/-150 um/propionic acid (3 g/kg)/sedigraph analysis



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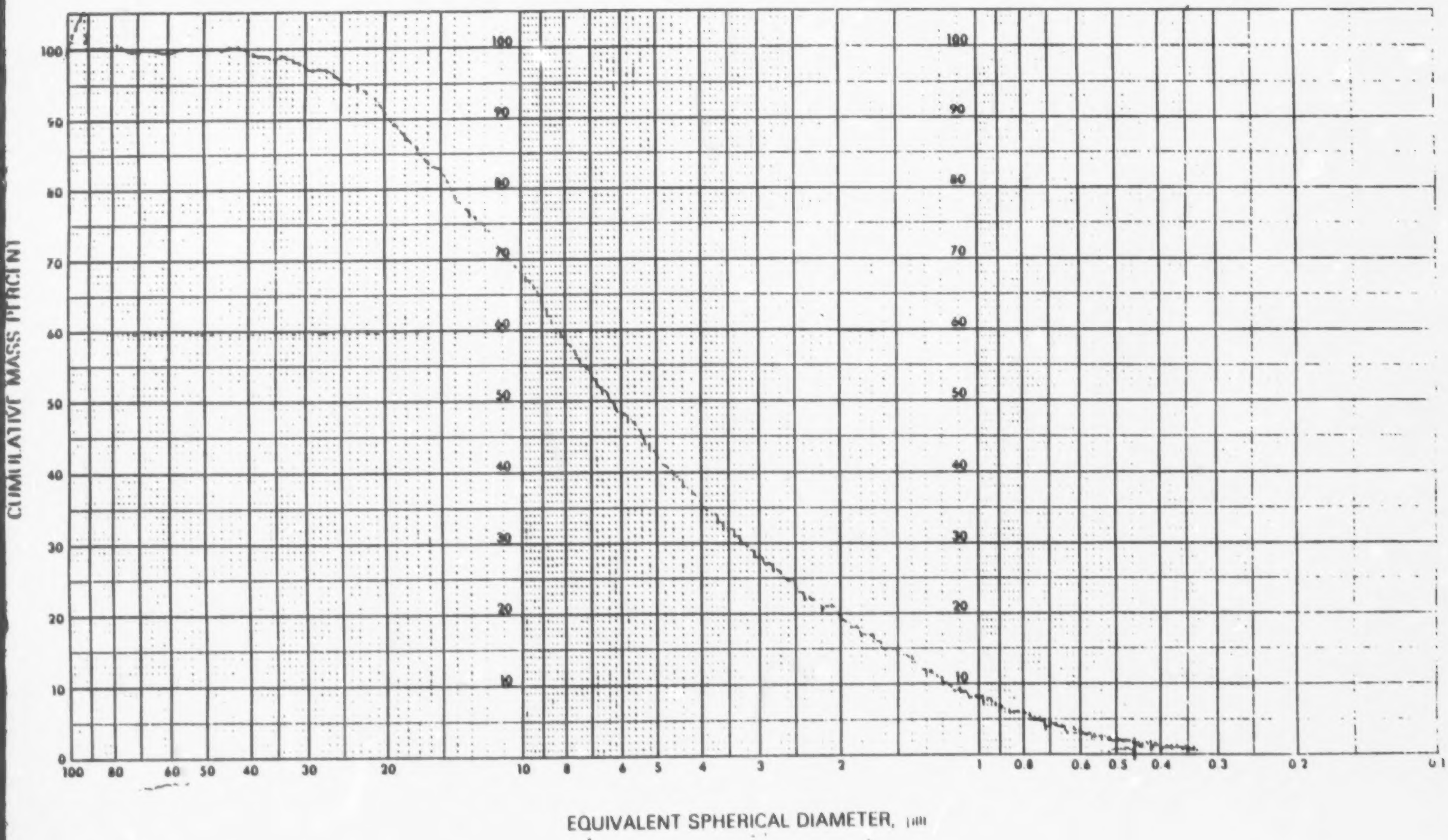
Organic grinding of calcite/70 min/0.5 kg/-150 um/propanol (3 g/kg)/sedigraph analysis



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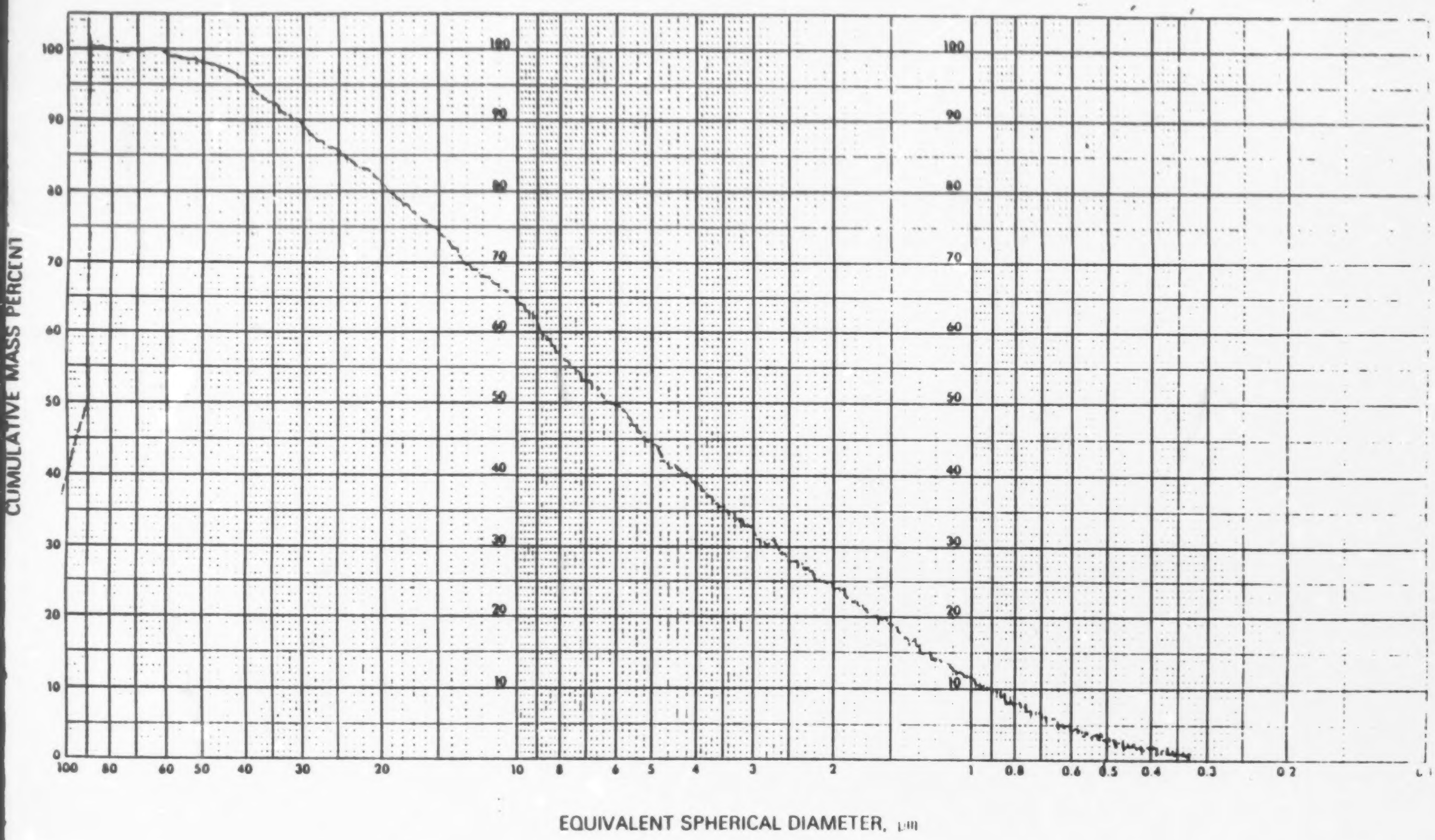
instrument corporation

Organic grinding of calcite/70 min/0.5 kg/-150 um/ether (3 g/kg)/sedigraphanalysis



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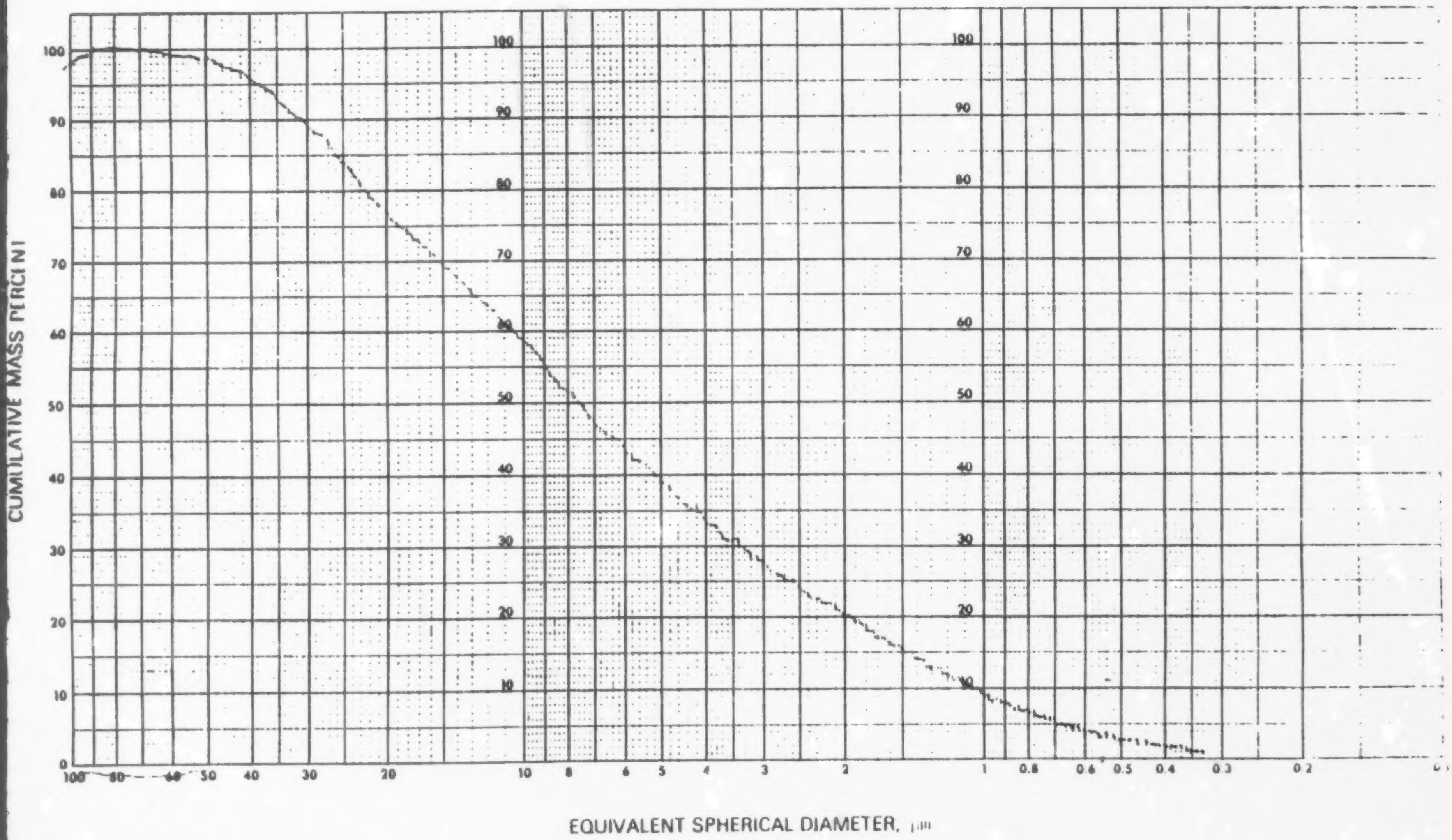
Organic grinding of calcite/70 min/0.5 kg/-150 um/ketone (3 g/kg)/sedigraph analysis



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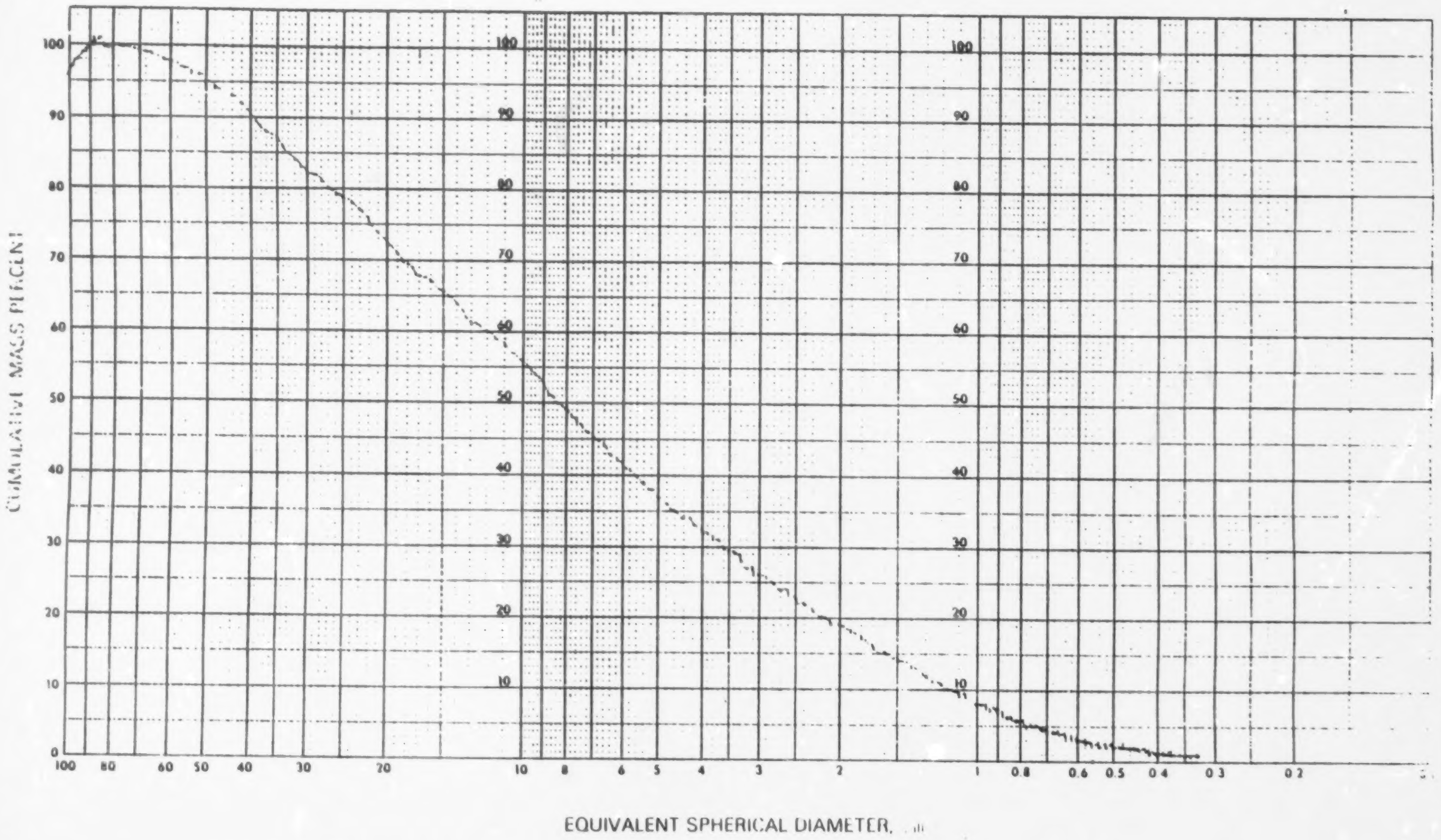
Organic grinding of calcite/70 min/0.5 kg/-150 um/kerosene (3 g/kg)/sedigraph analysis



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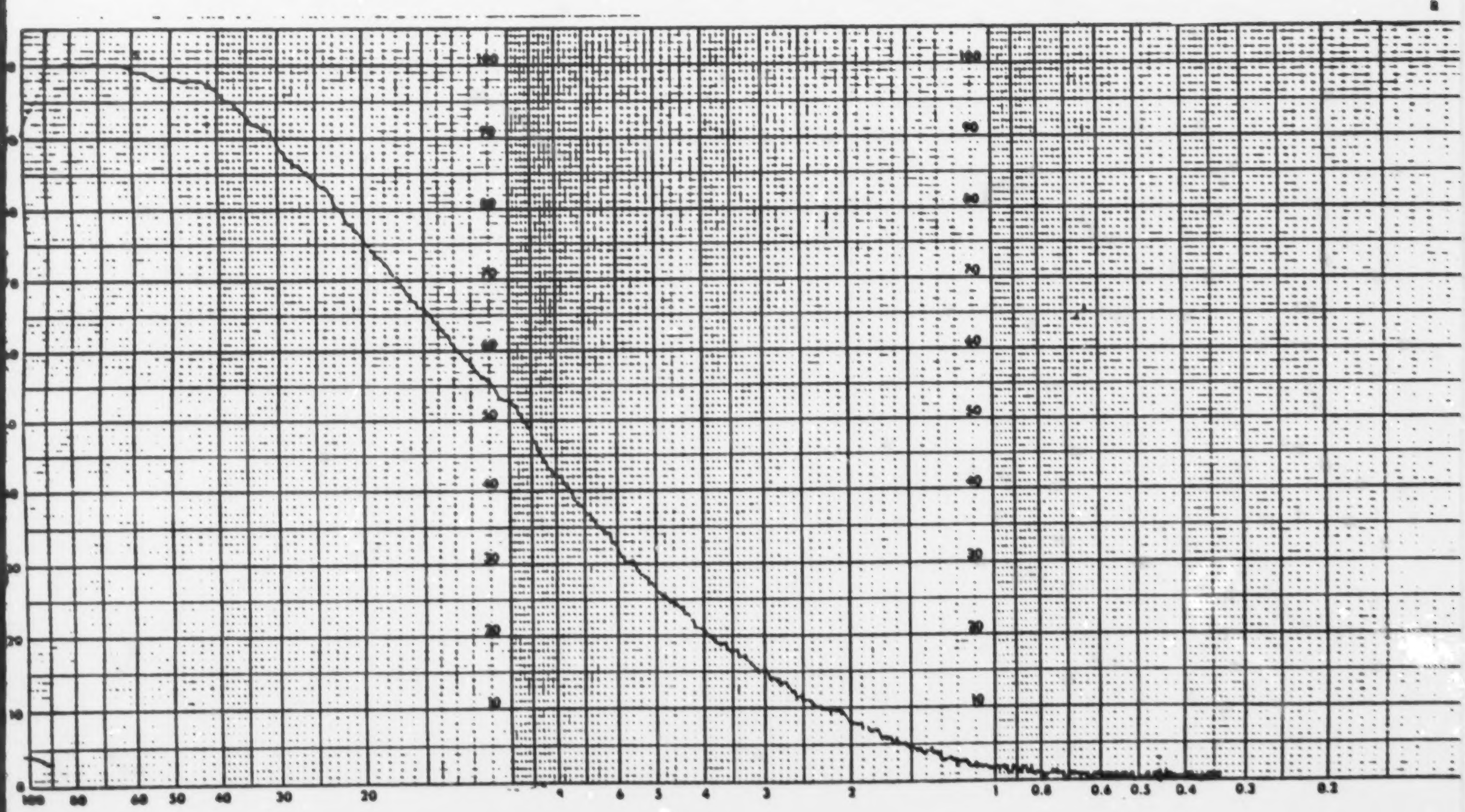
PARTICLE SIZE DISTRIBUTION

Organic grinding/calcite/0.5 kg/70 min/40 g/kg/propionic acid/sedigraph analysis



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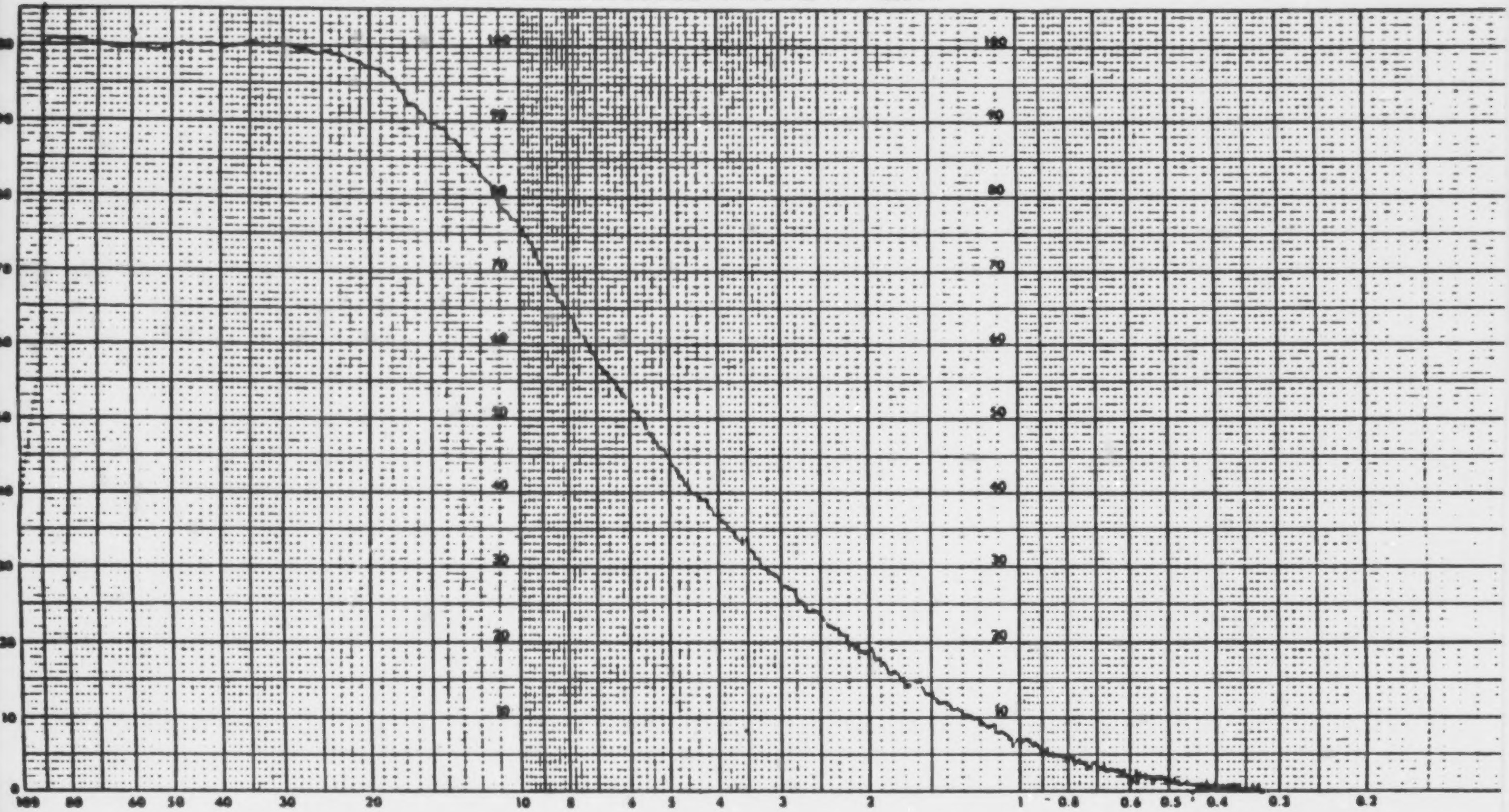
PARTICLE SIZE DISTRIBUTION

Organic grinding/calcite/0.5 kg/70 min/10 g/kg/propionic acid/sedigraph analysis



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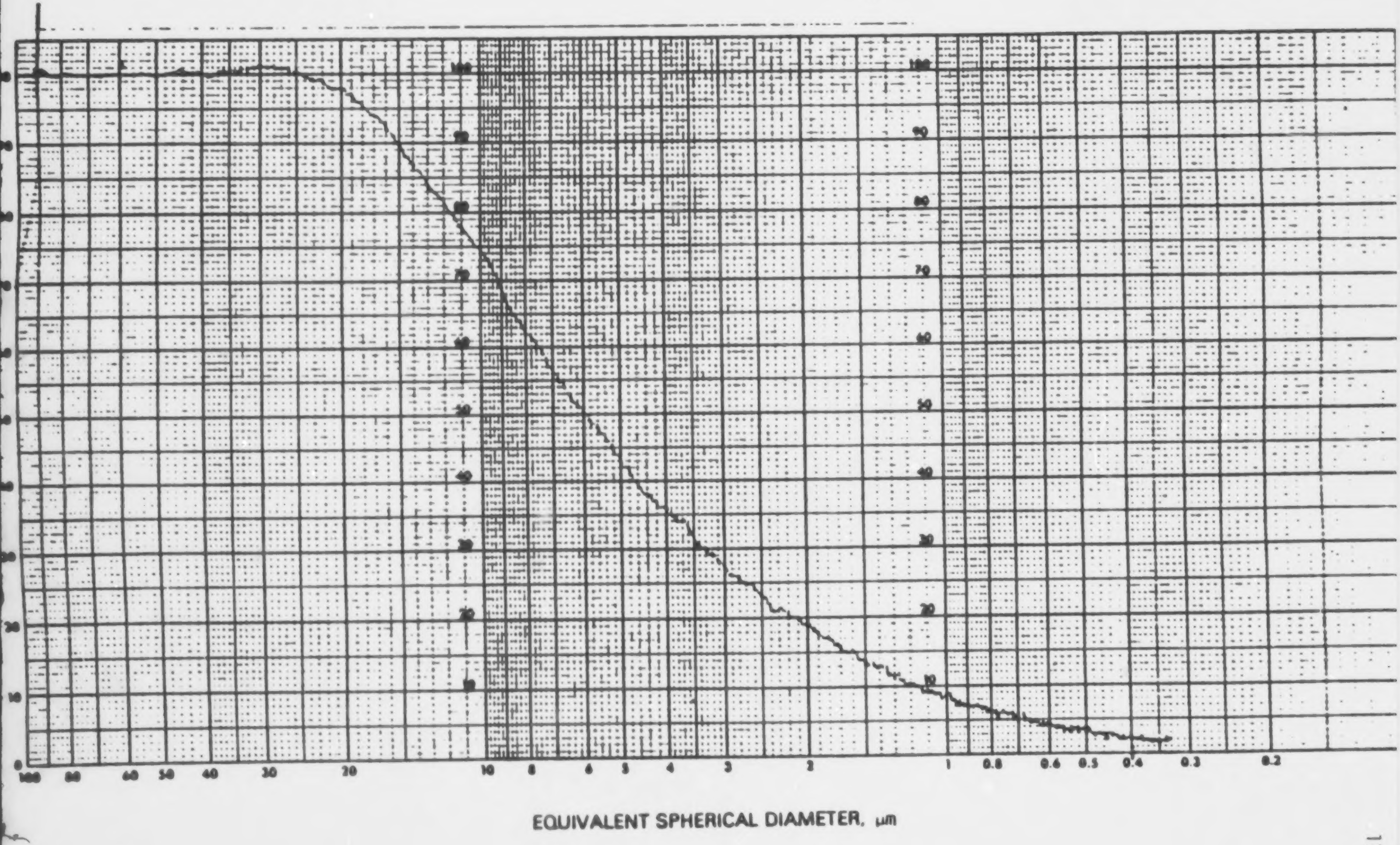
PARTICLE SIZE DISTRIBUTION

Organic grinding/calcite/0.5 kg/70 min/1.5 g/kg/propionic acid/sedigraph analysis



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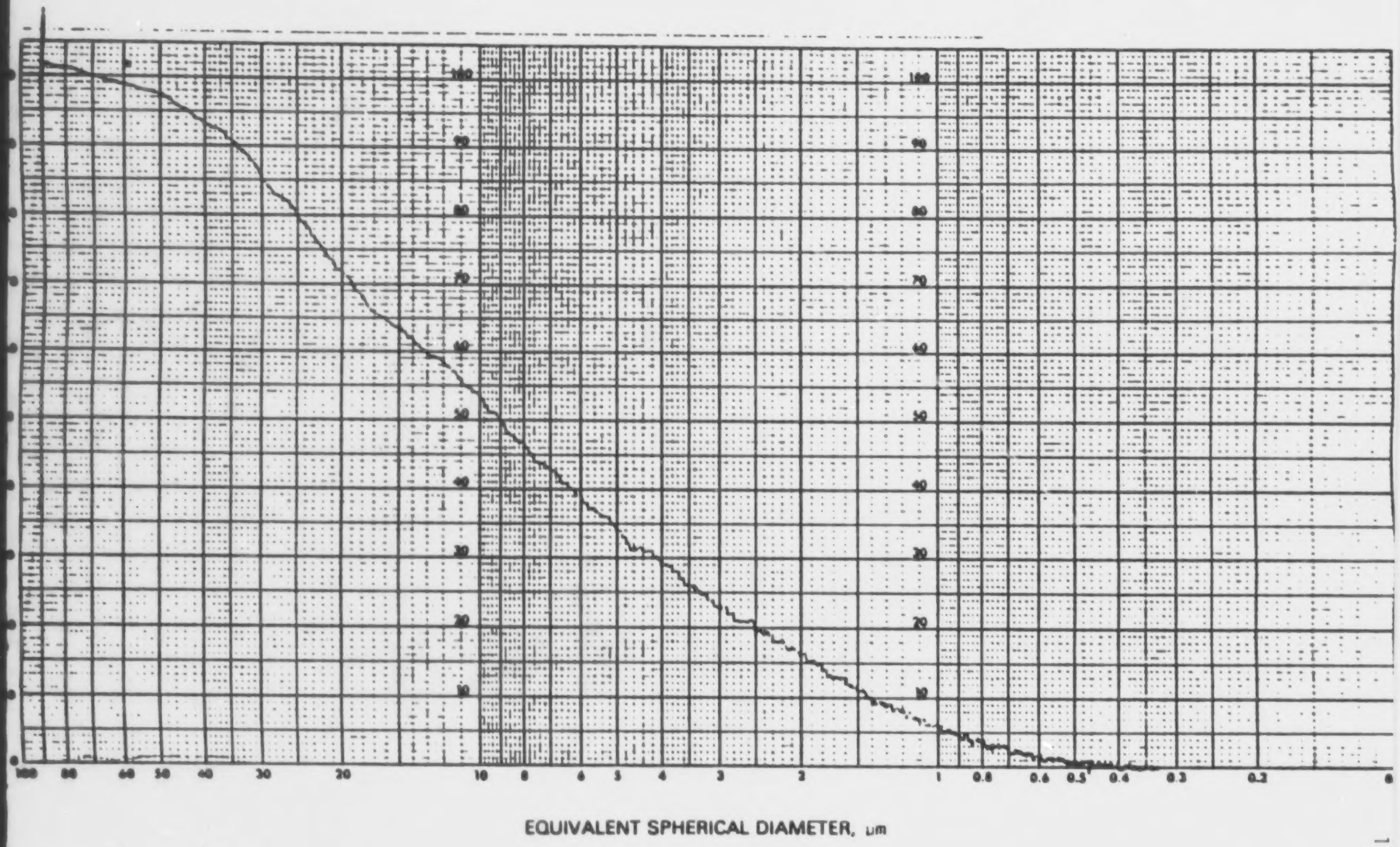
PARTICLE SIZE DISTRIBUTION

Organic grinding/calcite/10.5 kg/70 min/0.2 g/kg/propionic acid/sedigraph analysis



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ORGANIC GRINDING OF CALCITE, EFFECT ON ADDITION OF PROPIONIC ACID ON COARSE PARTICLES.

g/kg of added propionic acid	wt % passing 100 mesh
0	79.2
0.2	95.7
0.6	98.6
1.5	99.6
3.0	99.9
10.0	99.7
40.0	57.7

APPENDIX E

MICA (PHLOGOPITE) GRINDING

Screen Analysis of Phlogopite
Head Sample

mesh	wt % (on screen)	wt % passing
20	0.1	99.9
65	99.0	0.9
100	0.2	0.7
200	0.4	0.3
270	0.1	0.2
325	0.0	0.2
pan	0.2	--

Mill Calibration of Phlogopite
Screen Analysis

grinding time 60 min./1.5 kg mineral charge

mesh	wt % (on screen)	wt % passing
20	0.1	99.9
65	46.7	53.2
100	10.0	43.2
200	18.0	25.2
270	6.7	18.5
325	2.7	15.8
pan	15.8	--

Mill Calibration of Phlogopite
Screen Analysis

grinding time 30 min./1.5 kg mineral charge

mesh	wt % (on screen)	wt % passing
20	0.1	99.9
65	69.0	30.9
100	7.6	23.3
200	10.8	12.5
270	3.2	9.3
325	1.0	8.3
pan	8.3	--

Mill Calibration of Phlogopite
Screen Analysis

grinding time 15 min./1.5 kg mineral charge

mesh	wt % (on screen)	wt % passing
20	0.1	99.9
65	81.8	18.1
100	5.3	12.8
200	6.6	6.2
270	1.7	4.5
325	0.5	4.0
pan	4.0	--

Mill Calibration of Phlogopite
Screen Analysis

grinding time 60 min./1.0 kg mineral charge

mesh	wt % (on screen)	wt % passing
20	0.0	100
65	29.8	70.2
100	7.5	62.7
200	19.4	433
270	10.4	329
325	7.2	257
pan	25.7	--

Mill Calibration of Phlogopite
Screen Analysis

grinding time 30 min./1.0 kg mineral charge

mesh	wt % (on screen)	wt % passing
20	0.0	100
65	49.0	51.0
100	9.4	41.6
200	16.7	24.9
270	6.4	18.5
325	2.2	16.3
pan	16.3	--

Mill Calibration of Phlogopite
Screen Analysis

grinding time 15 min./1.0 kg mineral charge

mesh	wt % (on screen)	wt % passing
20	0.1	99.9
65	70.7	29.2
100	7.6	21.8
200	10.6	11.2
270	3.1	8.1
325	0.9	7.2
pan	7.2	--

Mill Calibration of Phlogopite
Screen Analysis

grinding time 60 min./0.5 kg mineral charge

mesh	wt % (on screen)	wt % passing
20	0.0	100
65	12.2	87.8
100	4.9	82.9
200	16.6	66.3
270	8.2	58.1
325	0.8	57.3
pan	57.3	--

Mill Calibration of Phlogopite
Screen Analysis

grinding time 30 min./0.5 kg mineral charge

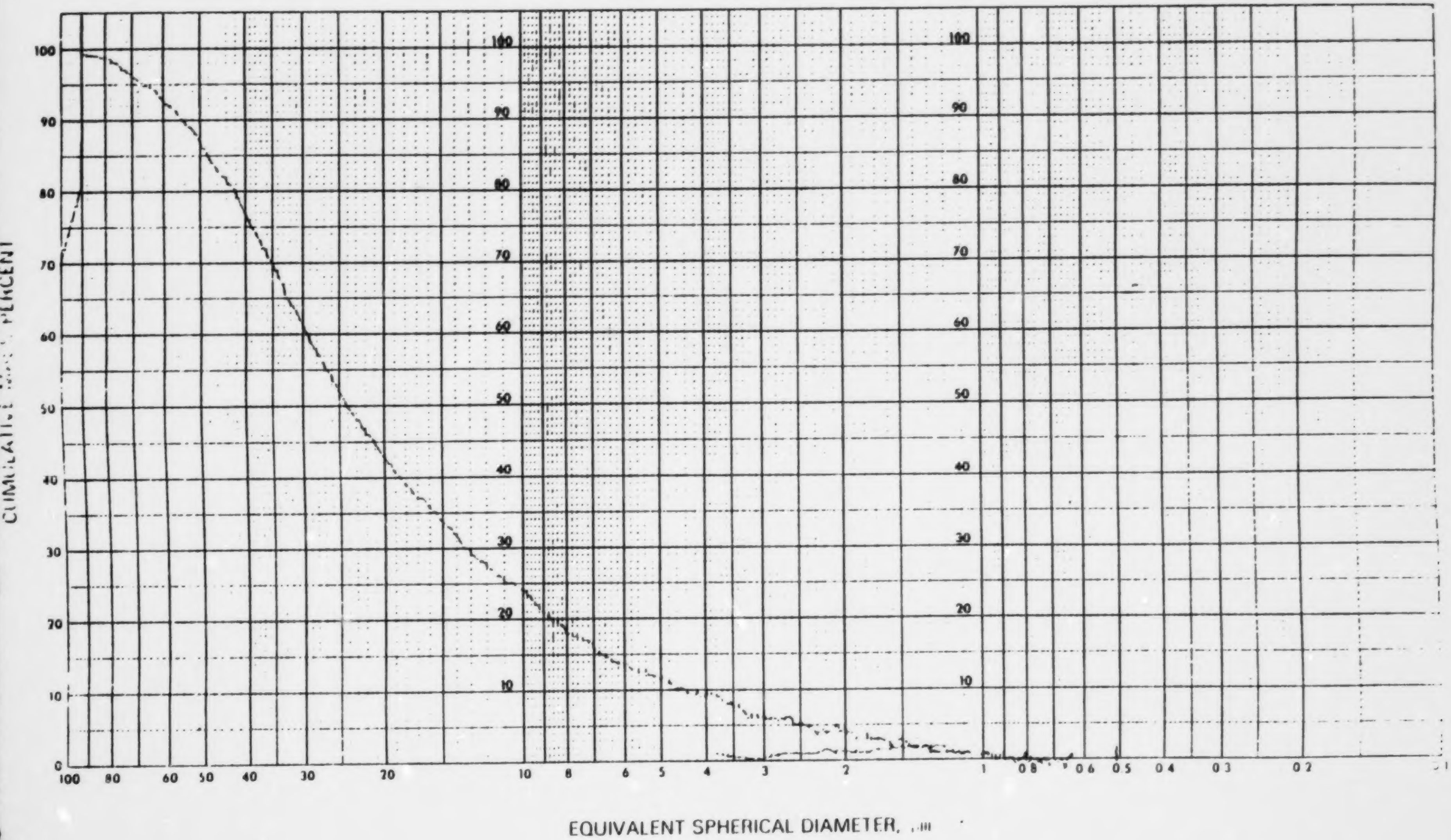
mesh	wt % (on screen)	wt % passing
20	0.0	100
65	28.7	71.3
100	6.3	65.0
200	16.0	49.0
270	8.9	40.1
325	4.7	35.4
pan	35.4	--

Mill Calibration of Phlogopite
Screen Analysis

grinding time 15 min./0.5 kg mineral charge

mesh	wt % (on screen)	wt % passing
20	0.1	99.9
65	45.5	54.4
100	7.8	46.6
200	16.0	30.6
270	7.3	23.3
325	2.2	21.1
pan	21.1	--

Organic grinding of phlogopite/25 min/0.5 kg/-150 um/blank/sedigraph analysis



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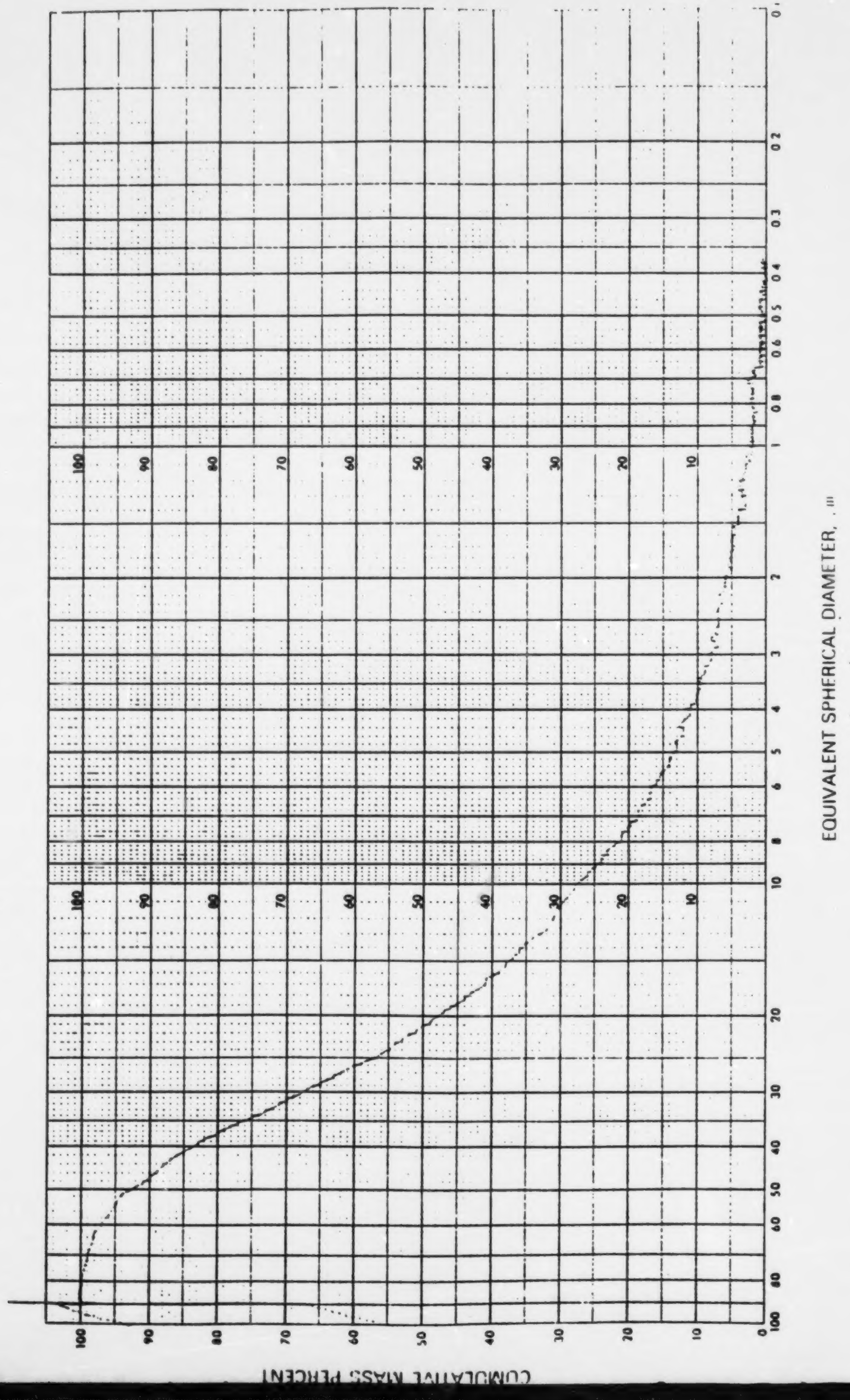
Organic grinding of phlogopite/25 min/0.5 kg/-150 um/propionic acid (3g/kg)/sedigraph analysis



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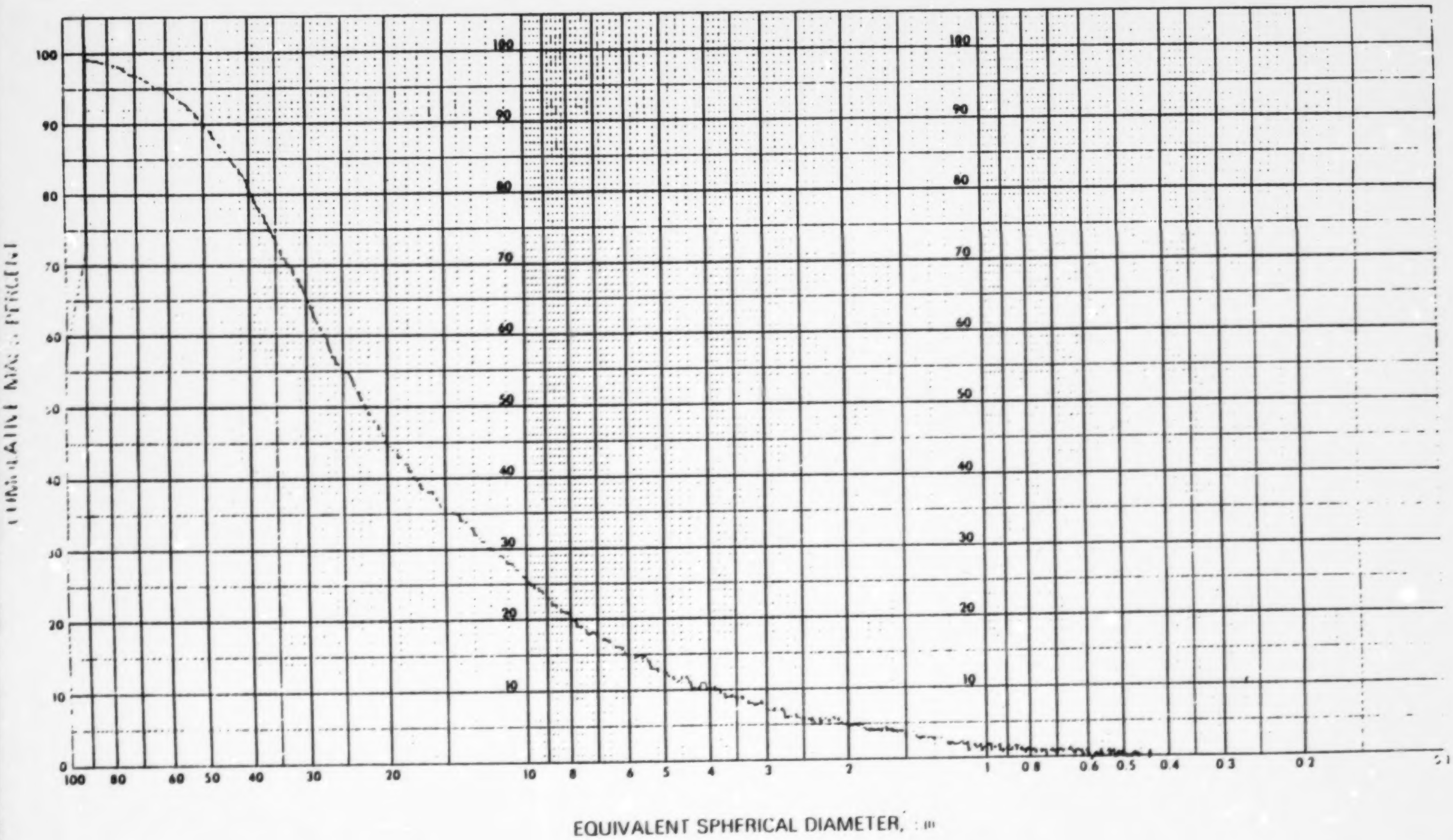
instrument corporation

Organic grinding of phlogopite/25 min/0.5 kg/-150 um/propanol (3 g/kg)/sedgraph analysis



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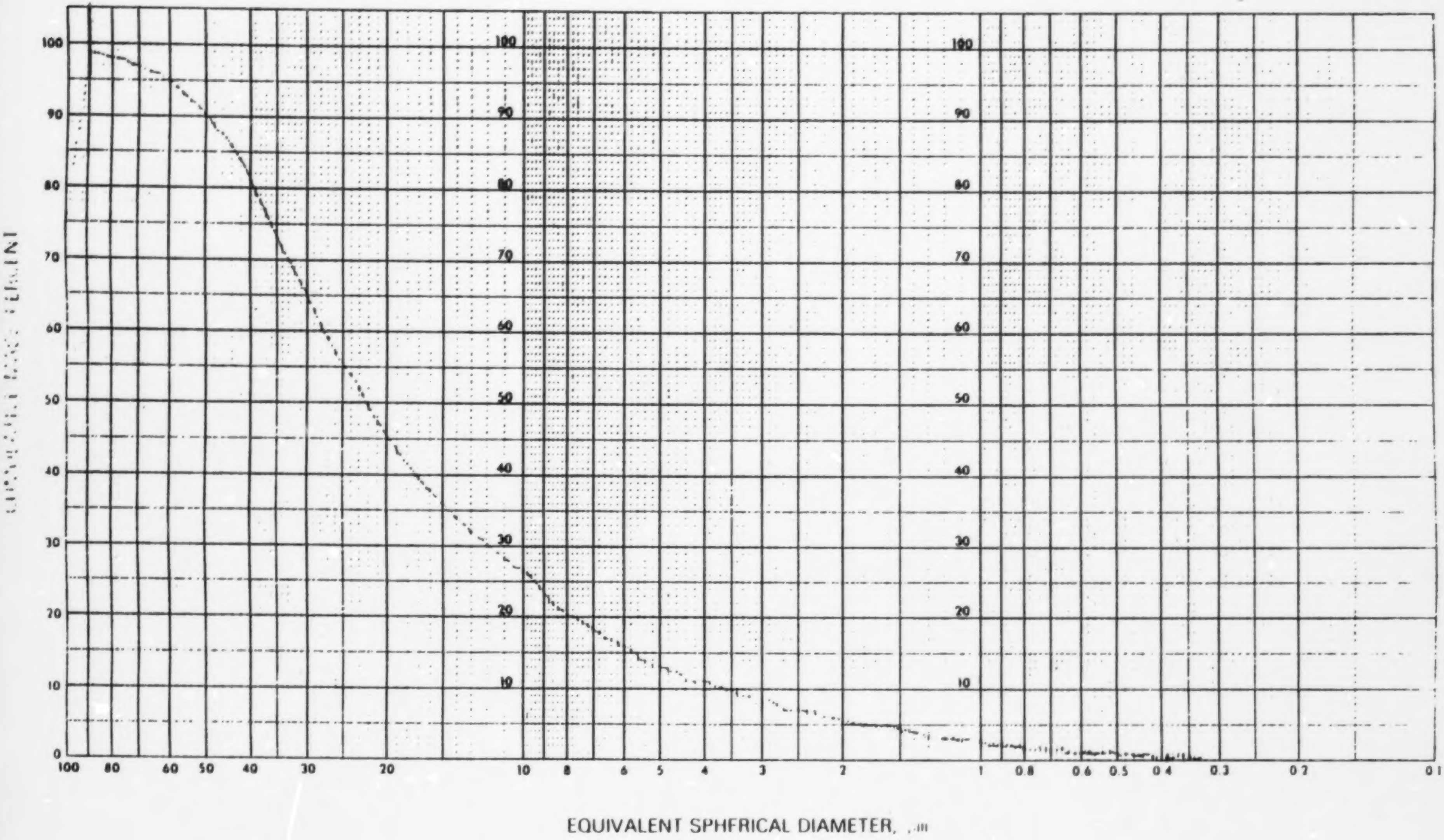
Organic grinding of phlogopite/25 min/0.5 kg/-150 um/ether (3 g/kg)/sedigraph analysis



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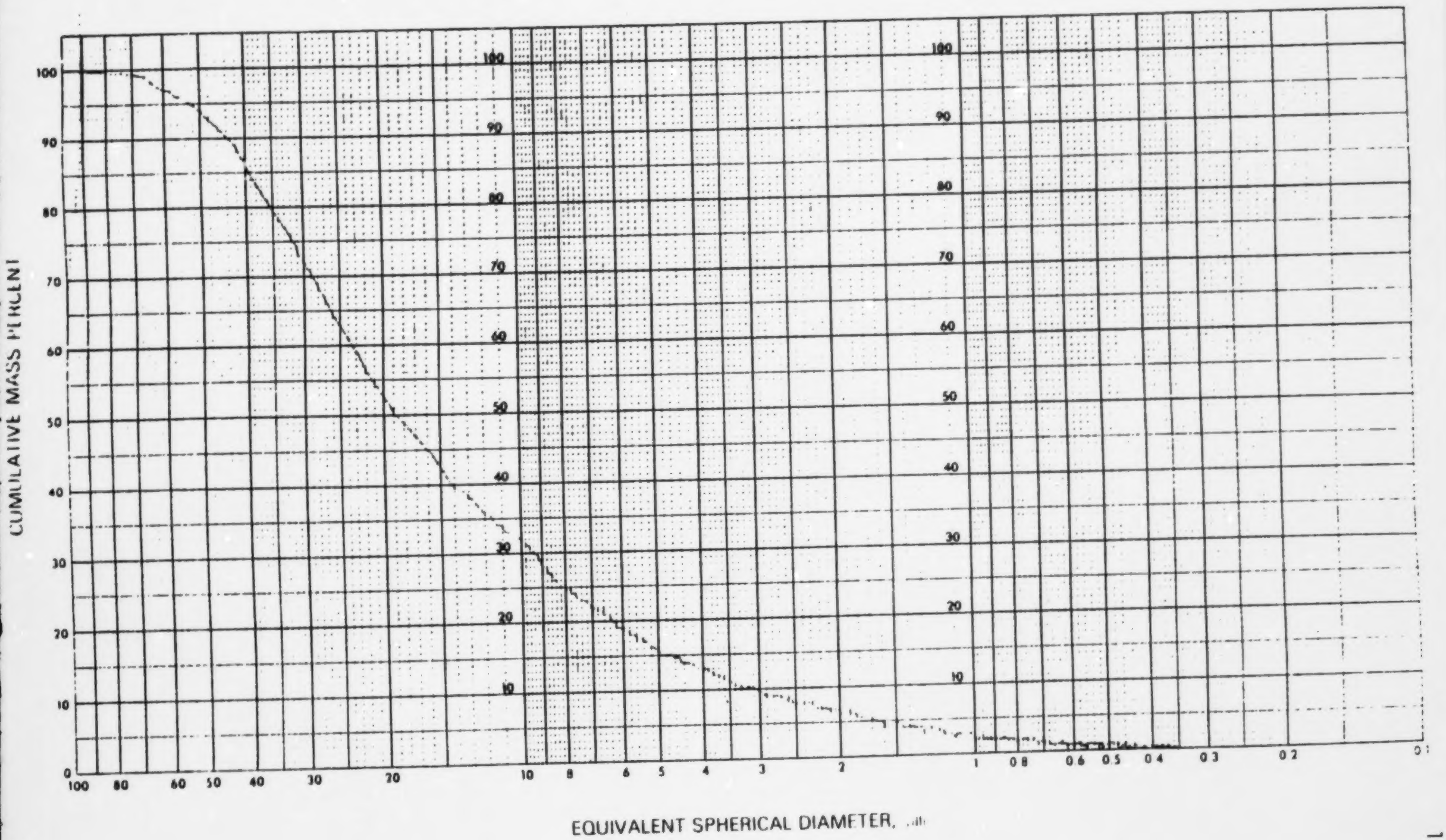
instrument corporation

Organic grinding of phlogopite/25 min/0.5 kg/-150 um/ketone (3 g/kg)/sedigraph analysis



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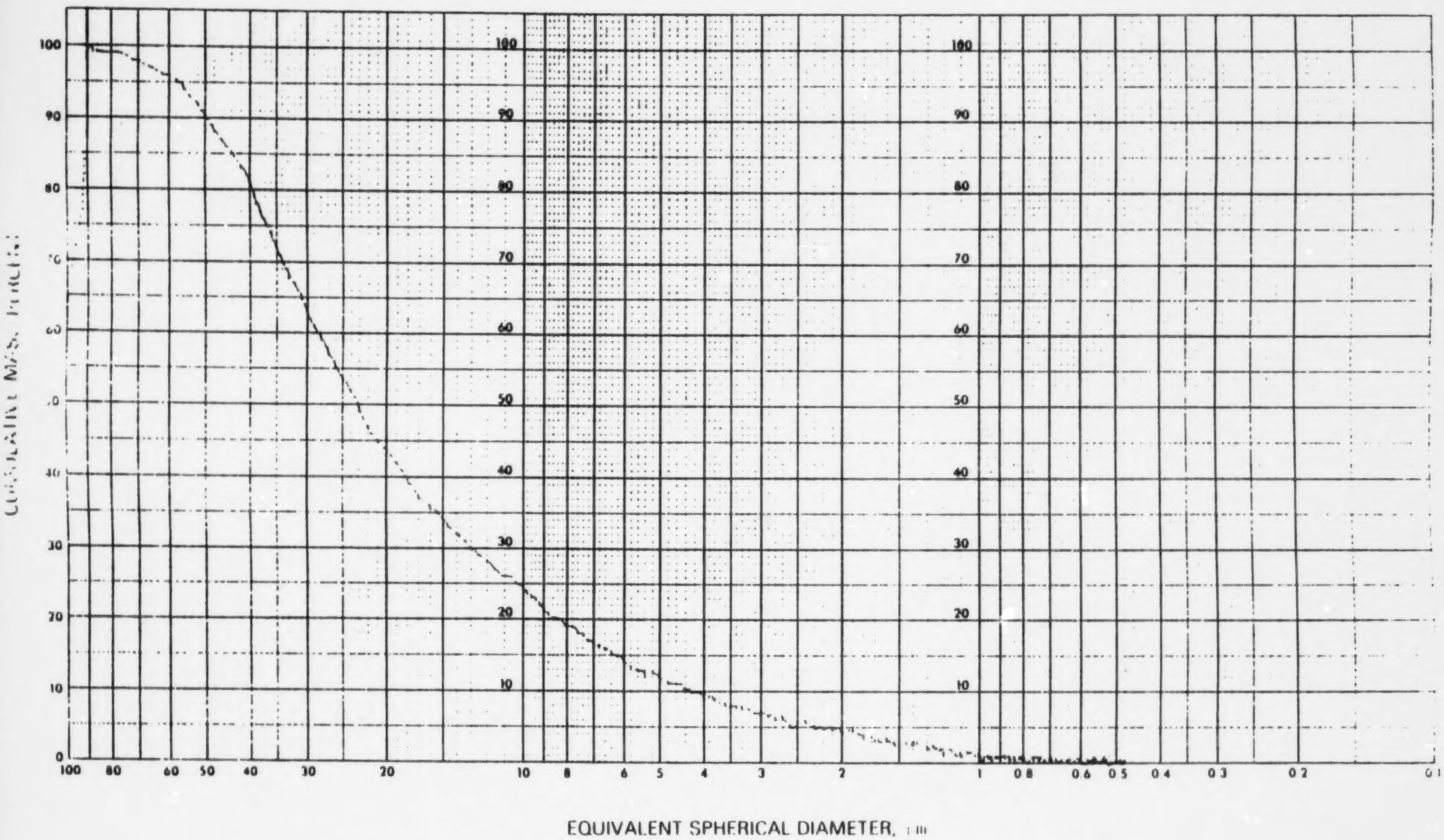
instrument corporation

Organic grinding of phlogopite/25 min/0.5 kg/-150 um/kerosene (3 g/kg)/sedigraph analysis



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instrument corporation

ORGANIC GRINDING OF PHLOGOPITE EFFECT ON COARSE PARTICLES

additive	wt % passing 100 mesh
----*)	55.5
propanol	52.0
propionic acid	57.1
ether	39.4
ketone	50.5
kerosene	41.0

*) blank

APPENDIX F

INFRARED (and TGA) ANALYSIS OF TEST PRODUCTS AND COMMERCIAL REFERENCE MATERIALS

April 8, 1988

Gerhard Heinrich
MRCCR

REPORT NUMBER:	PC 479-88-1
IDENTIFICATION:	Work Order No. 27817
SPECIFICATIONS	Diffuse Reflectance Infrared (DRIFT) analysis of samples submitted

---

INTRODUCTION

A series of mineral powders (some coated, some uncoated) were submitted for comparative diffuse reflectance infrared (DRIFT) analysis in order to determine if differences could be detected due to the presence of the coatings.

EXPERIMENTAL

The samples were diluted with KBr powder and analyzed using an Analect FX-6160 Fourier Transform Infrared (FTIR) Spectrometer equipped with an FXA-530 Aspheric IR reflectance accessory.

For comparison, two of the samples (one coated, one uncoated) were also pressed into KBr pellets for transmission infrared analysis.

Thermal gravimetric analysis (TGA) was also carried out on these two materials in order to determine if significant differences due to the coating could be detected. Analysis was carried out using a Dupont 951 TGA controlled by a 9900 computer programmer. Samples were heated from room temperature to 1000°C at 10°C/min in an atmosphere of nitrogen flowing at 100cc/min.

RESULTS

A summary of samples submitted and scans carried out is included in Table I.

No significant differences were detected between comparable coated and uncoated samples by DRIFT, Transmission IR, or TGA in the testing carried out. Most likely due to the very low concentration of coating apparently present (0.3% to 1.0% by weight).

DISCUSSION

Other analytical techniques which might be feasible include x-ray fluorescent for inorganic constituents of coatings such as silicon.

Organic coatings might be detected by chemical removal or volitization followed by gas chromatography/mass spectrometry (GC/MS). Otherwise surface techniques such as Auger spectroscopy would be required.

L. Chu

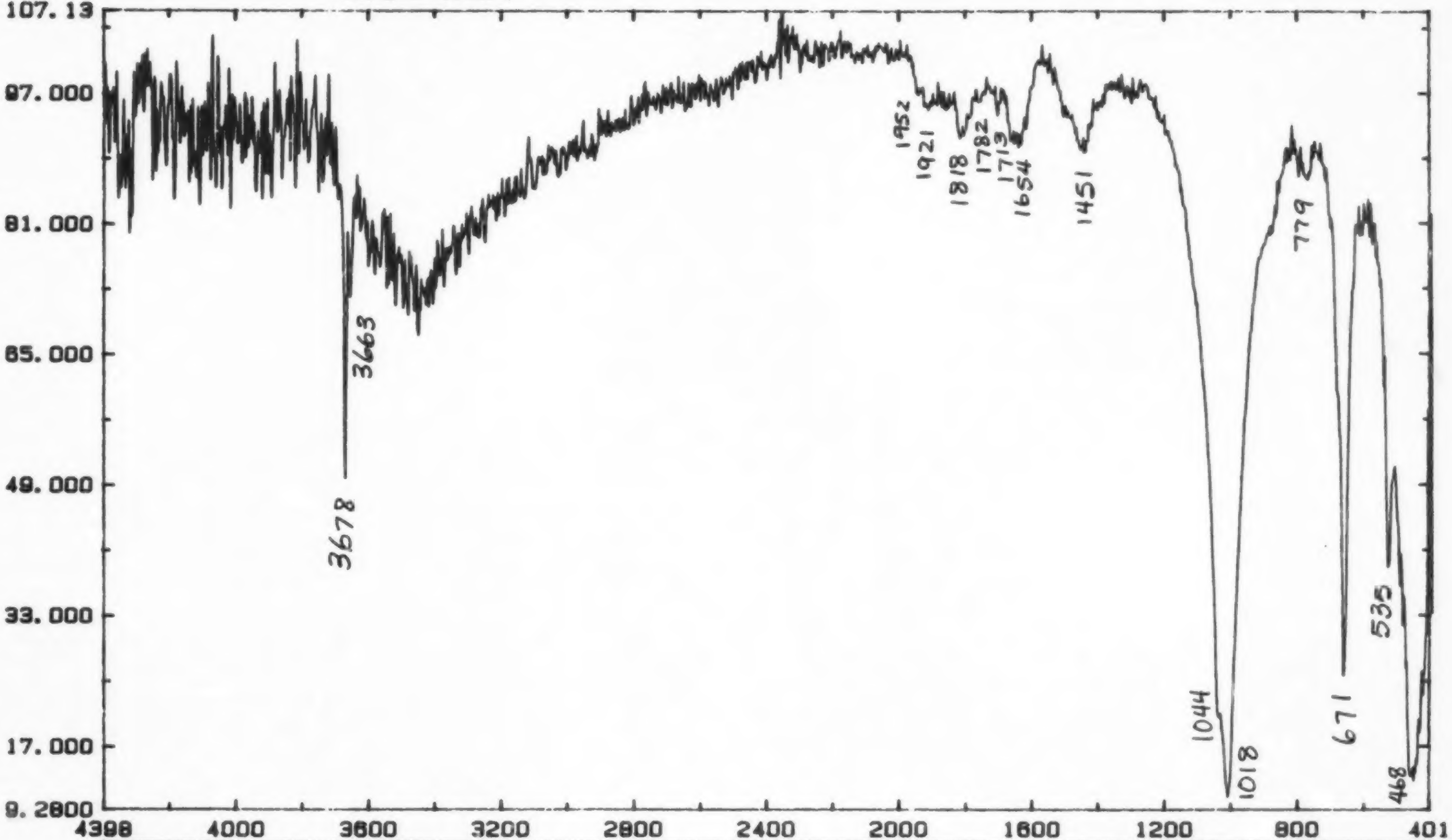
Lily Chu
Project Technologist

John Moore

John Moore, Ph.D
Project Scientist

IR Spectrum No.	Sample No.	Description	Comments
1	G157	Talc	
2	G158	Talc, coated	Identical to Spectrum #1
3	G159	Talc/ref./-44-26	
4	G160	Talc/ref./coated 1200	Identical to Spectrum #3
5A	G161	Calcite/-	
5B	G161	Calcite/-, (KBr pellet)	Peaks broad compared to DRIFT
6A	G162	Calcite/coated	Identical to Spectrum #5A - slightly smaller peak at 1081 cm^{-1}
6B	G162	Calcite/coated, (KBr pellet)	Identical to Spectrum #5B
7	G163	Calcite/ref./-15-15	Band at 1013 cm^{-1} smaller, as in Spectrum #6A
8	G164	Calcite/ref./coated 40_2	Identical to Spectrum #7
9	G165	Sazorite/-	
10	G166	Sazorite/coated	Identical to Spectrum #9 - slightly smaller peak at 1440 cm^{-1}
11	G167	SiO_2/-	
12	G168	SiO_2/coated	Identical to Spectrum #11
TGA Scan No.			
1	G163	Calcite/ref./-15-15	wt% remaining, 500°C : 100% 1000°C : 56.52%
2	G164	Calcite/ref./coated 40_2	wt% remaining, 500°C : 99.88% 1000°C : 57.33%

SPECTRUM #1

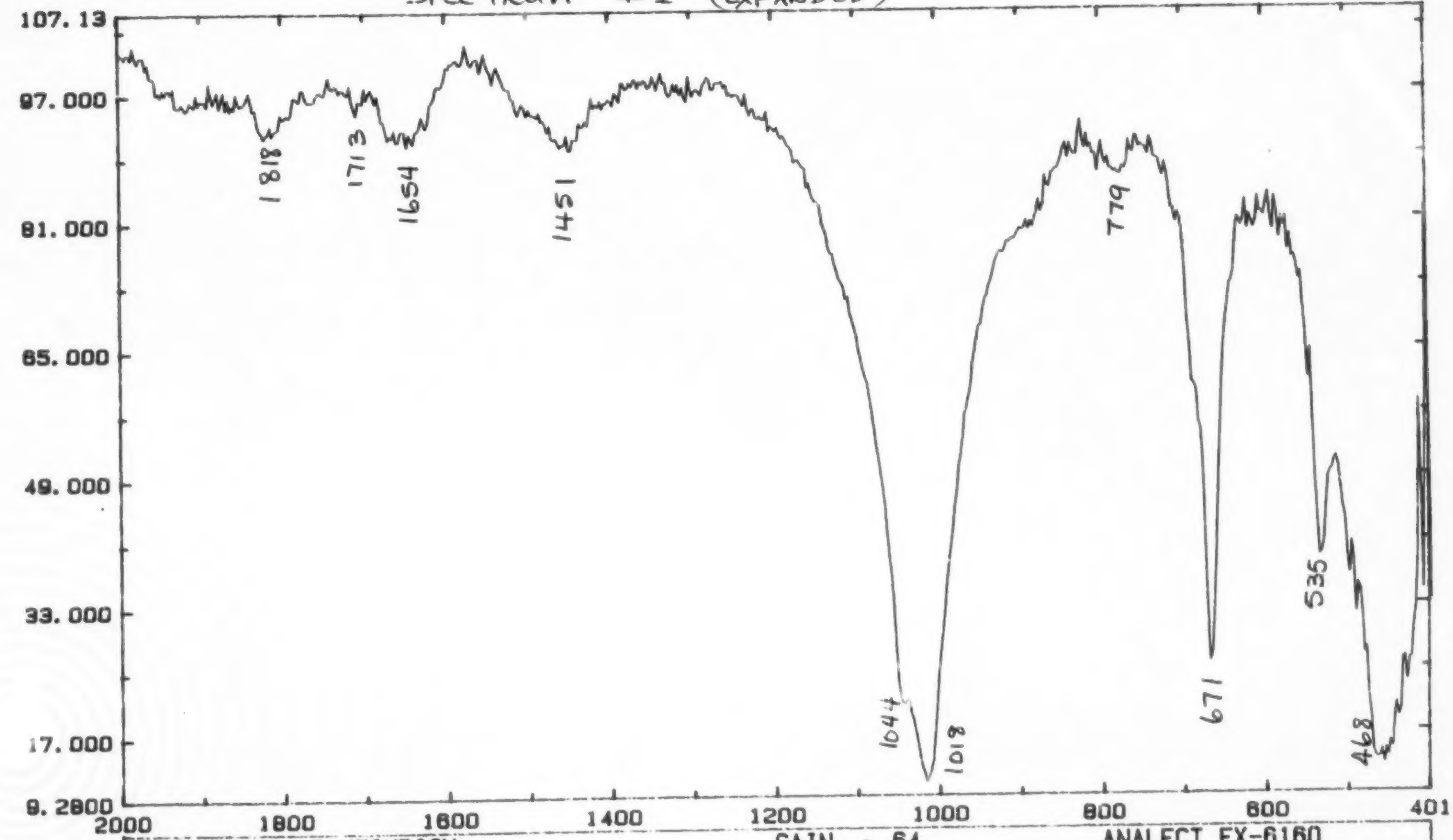


FILE NAME : G.HEINRICH
#SCANS : 300
#BKG : 64
APOD : HAPP-GENZEL
COMMENT : DRIFT SAMPLE G157-TALC

GAIN : 64
DET : TGS
RES : 4 CM-1
DATE :

ANALECT FX-6160
ORD : %T
ABSC: WAVENUMBER
TIME:

SPECTRUM #1 (EXPANDED)

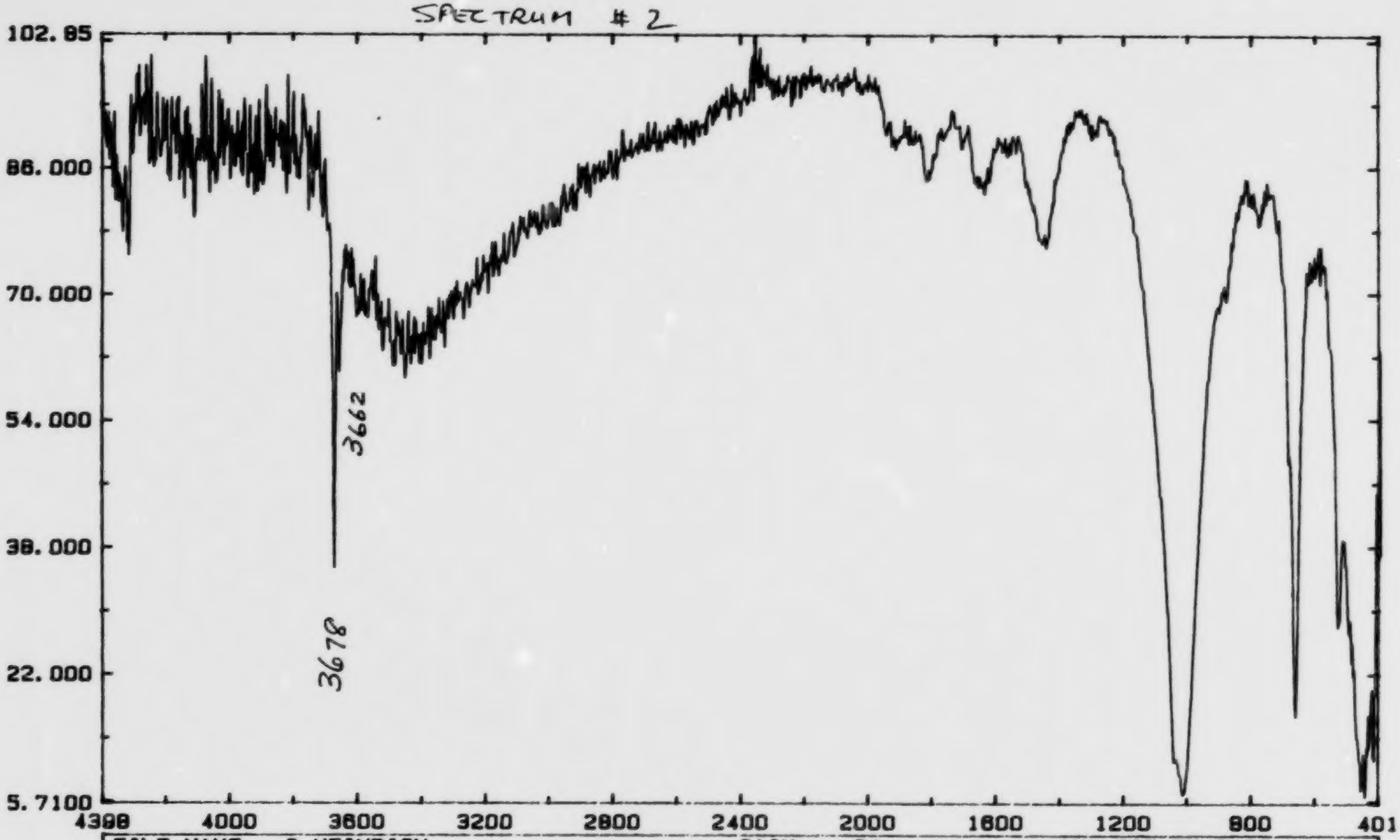


FILE NAME : G.HEINRICH
#SCANS : 300
#BKG : 64
APOD : HAPP-GENZEL
COMMENT : DRIFT SAMPLE G157-TALC

GAIN : 64
DET : TGS
RES : 4 CM-1
DATE :

ANALECT FX-6160
ORD : %T
ABSC: WAVENUMBER
TIME:

SPECTRUM # 2

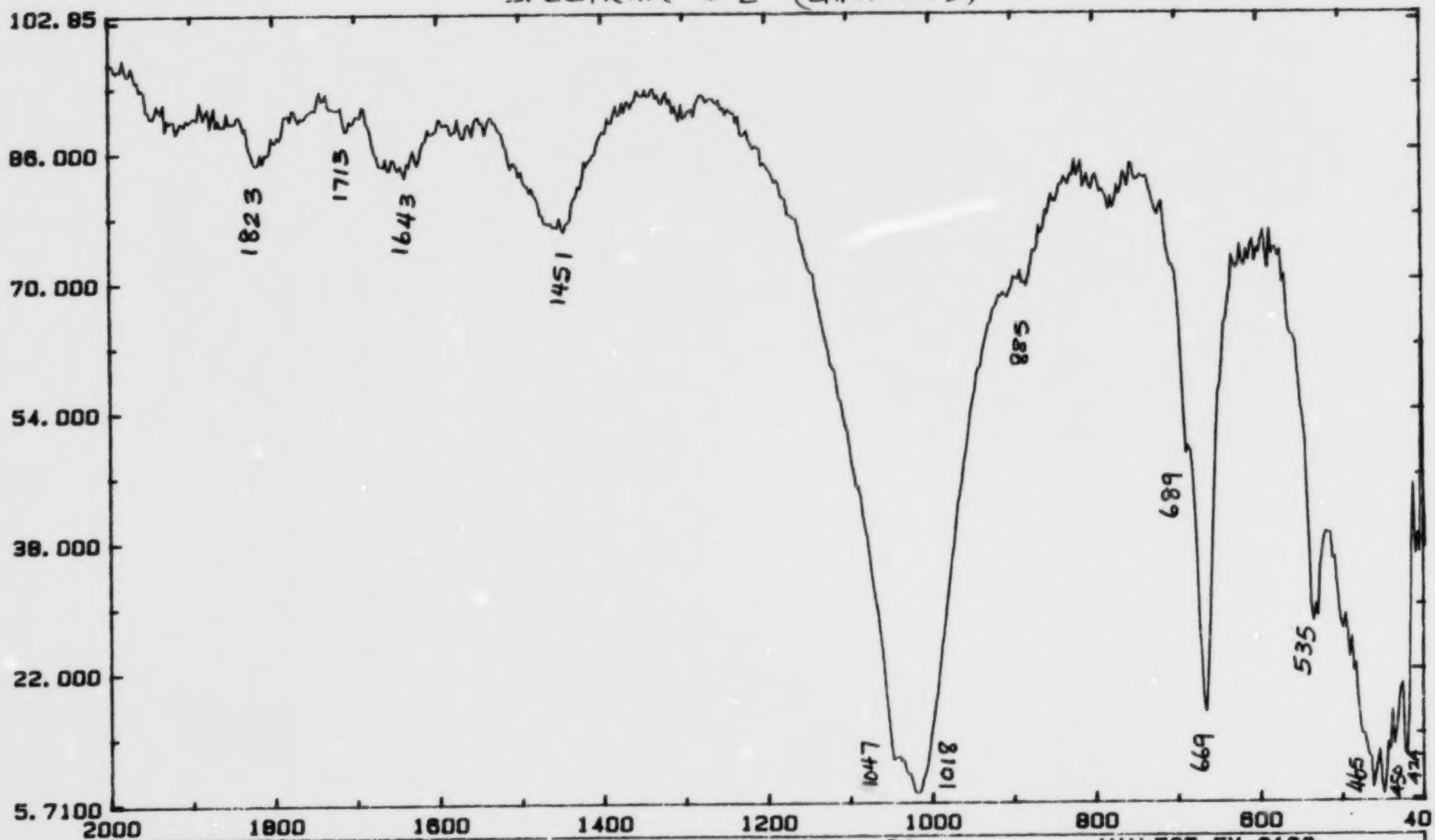


FILE NAME : G.HEINRICH
#SCANS : 300
#BKG : 64
APOD : HAPP-GENZEL
COMMENT : DRIFT SAMPLE G158-TALC, COATED

GAIN : 64
DET : TGS
RES : 4 CM-1
DATE :

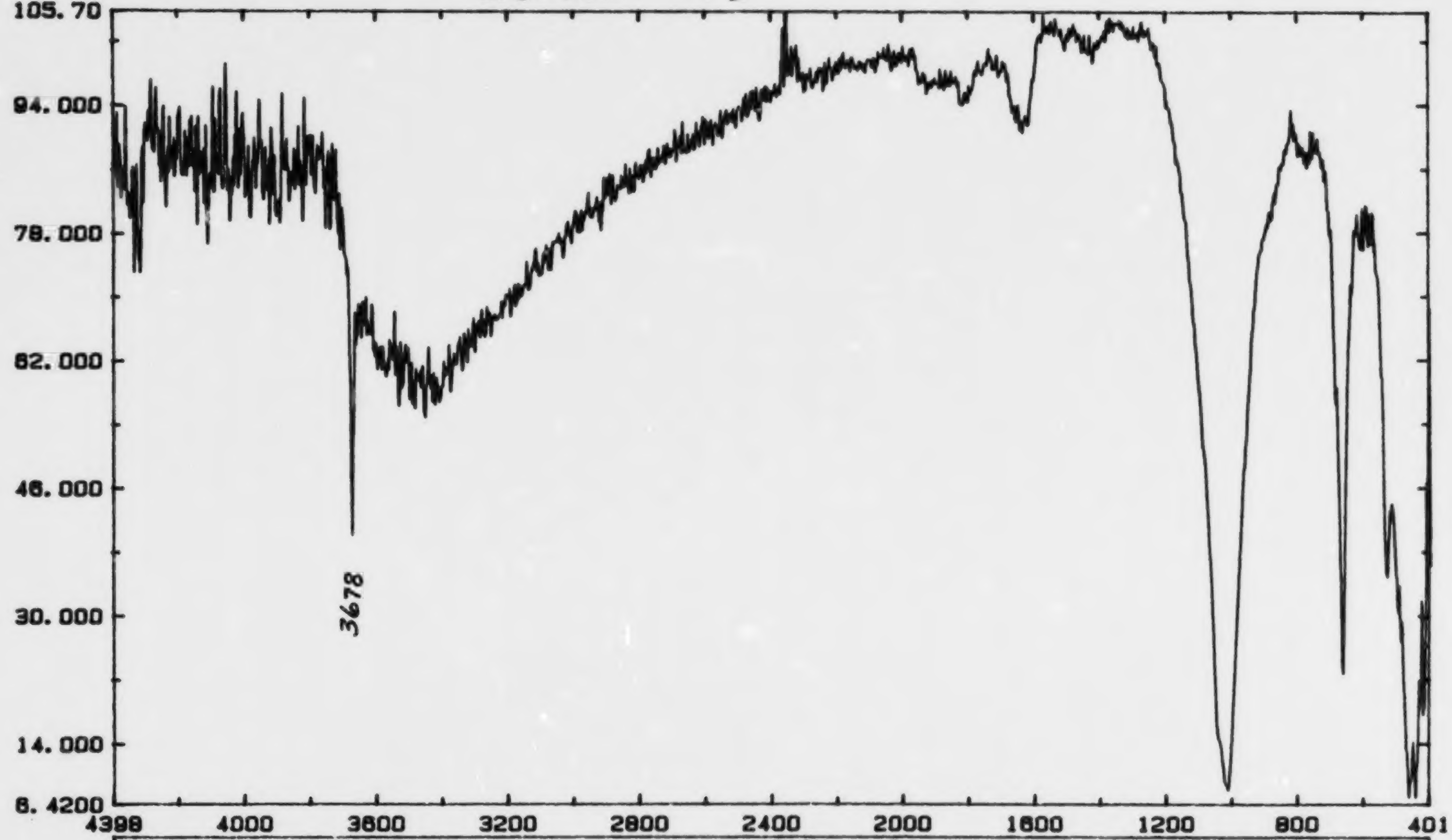
ANALECT FX-6160
ORD : %T
ABSC: WAVENUMBER
TIME:

SPECTRUM #2 (EXPANDED)



FILE NAME	G. HEINRICH	GAIN	64	ANALECT FX-6160		
#SCANS	300	DET	TGS	ORD : %T		
#BKG	64	RES	4 CM-1	ABSC: WAVENUMBER		
APOD	HAPP-GENZEL	DATE		TIME:		
COMMENT	DRIFT SAMPLE G158-TALC, COATED					

SPECTRUM #3

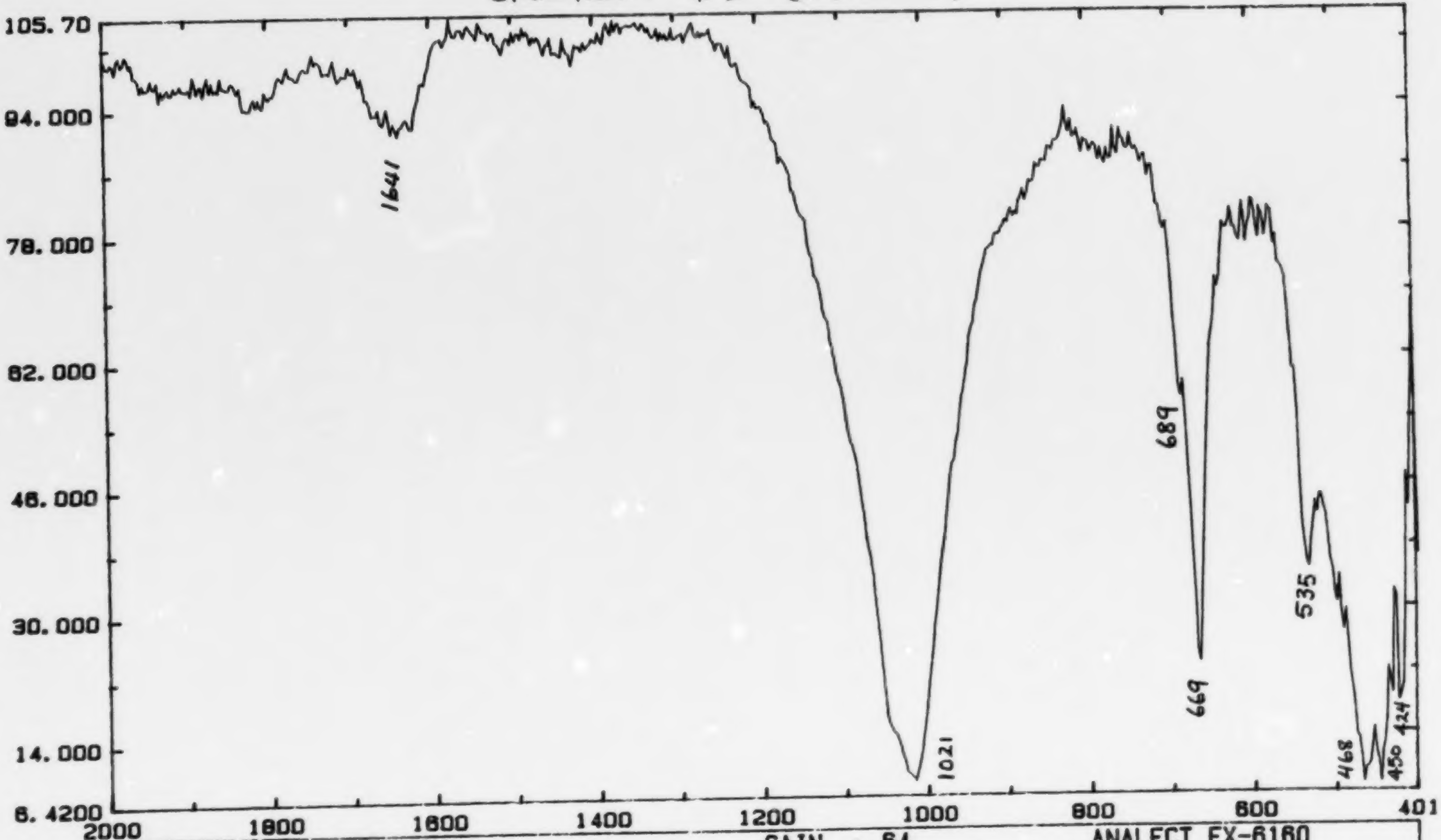


FILE NAME : G.HEINRICH
#SCANS : 300
#BKG : 64
APOD : HAPP-GENZEL
COMMENT : DRIFT SAMPLE G159: TALC/REF./44-26

GAIN : 64
DET : TGS
RES : 4 CM-1
DATE :

ANALECT FX-6160
ORD : %T
ABSC: WAVENUMBER
TIME:

SPEZTRUM #3 (EXPANDED)

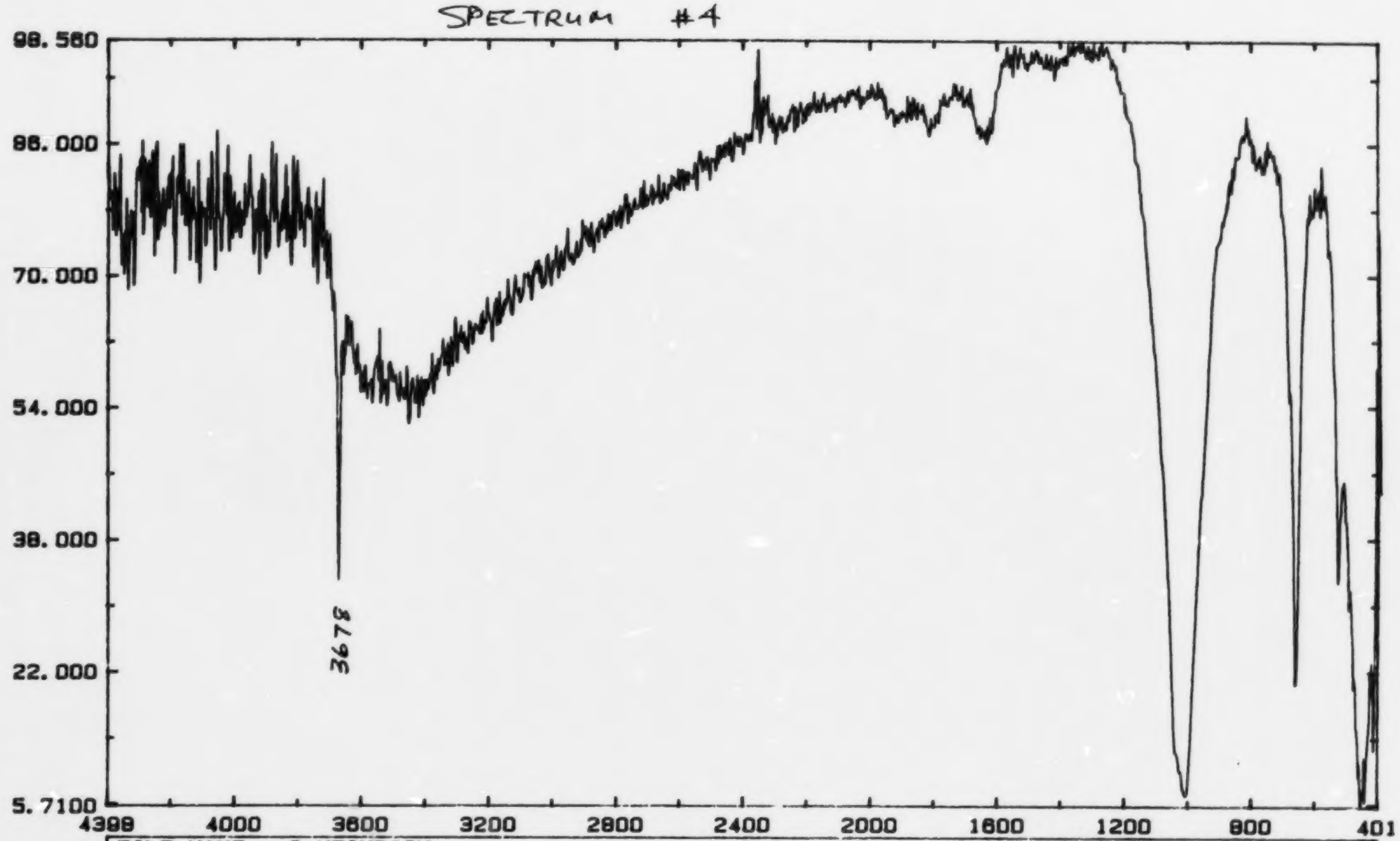


FILE NAME : G.HEINRICH
#SCANS : 300
#BKG : 64
APOD : HAPP-GENZEL
COMMENT : DRIFT SAMPLE G159: TALC/REF./44-26

GAIN : 64
DET : TGS
RES : 4 CM-1
DATE :

ANALECT FX-6160
ORD : %T
ABSC: WAVENUMBER
TIME:

SPECTRUM #4

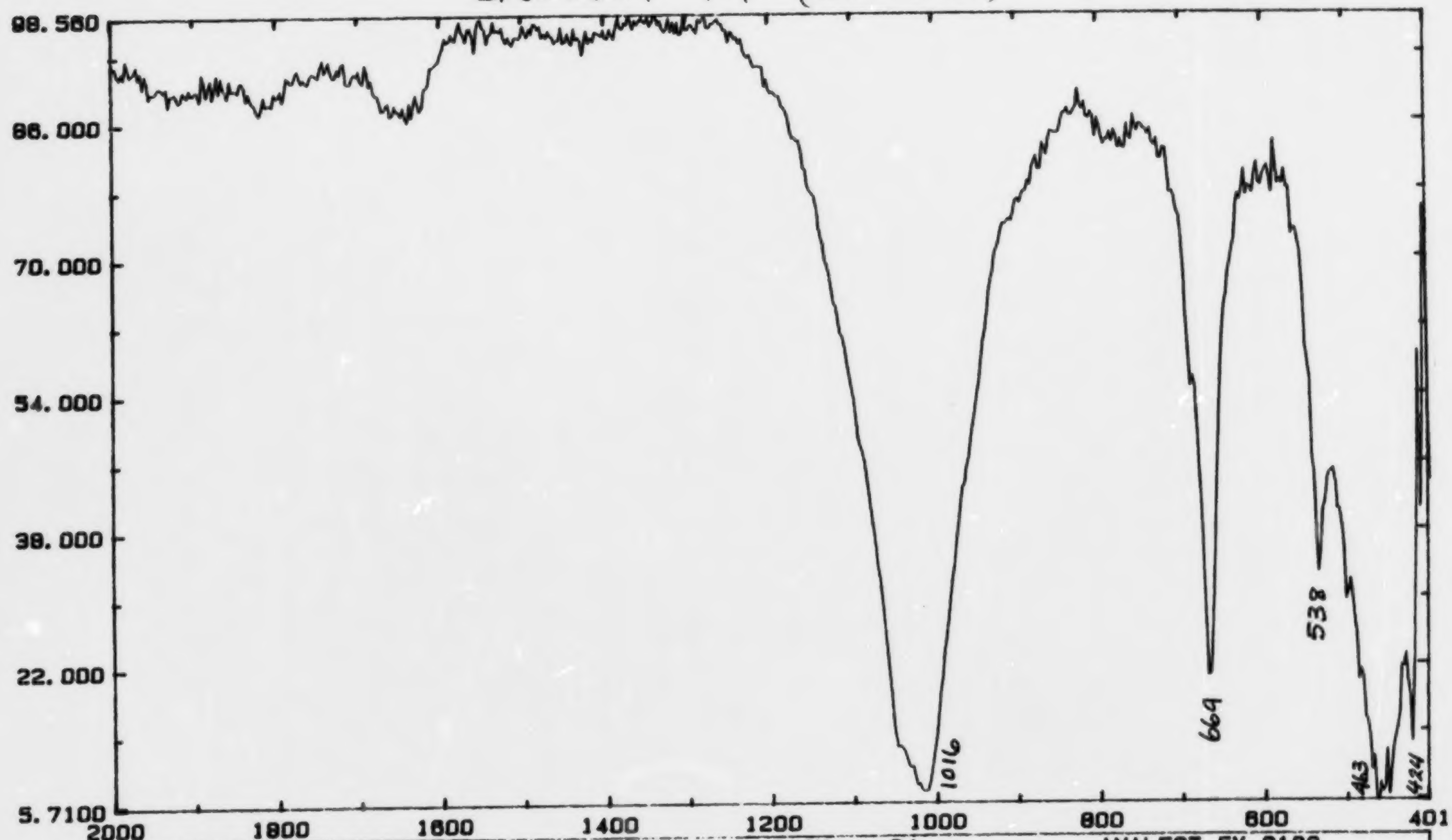


FILE NAME : G. HEINRICH
#SCANS : 300
#BKG : 64
APOD : HAPP-GENZEL
COMMENT : DRIFT SAMPLE G160: TALC/REF./COATED 1200

GAIN : 64
DET : TGS
RES : 4 CM-1
DATE :

ANALECT FX-6160
ORD : %T
ABSC: WAVENUMBER
TIME:

SPECTRUM #4 (EXPANDED)

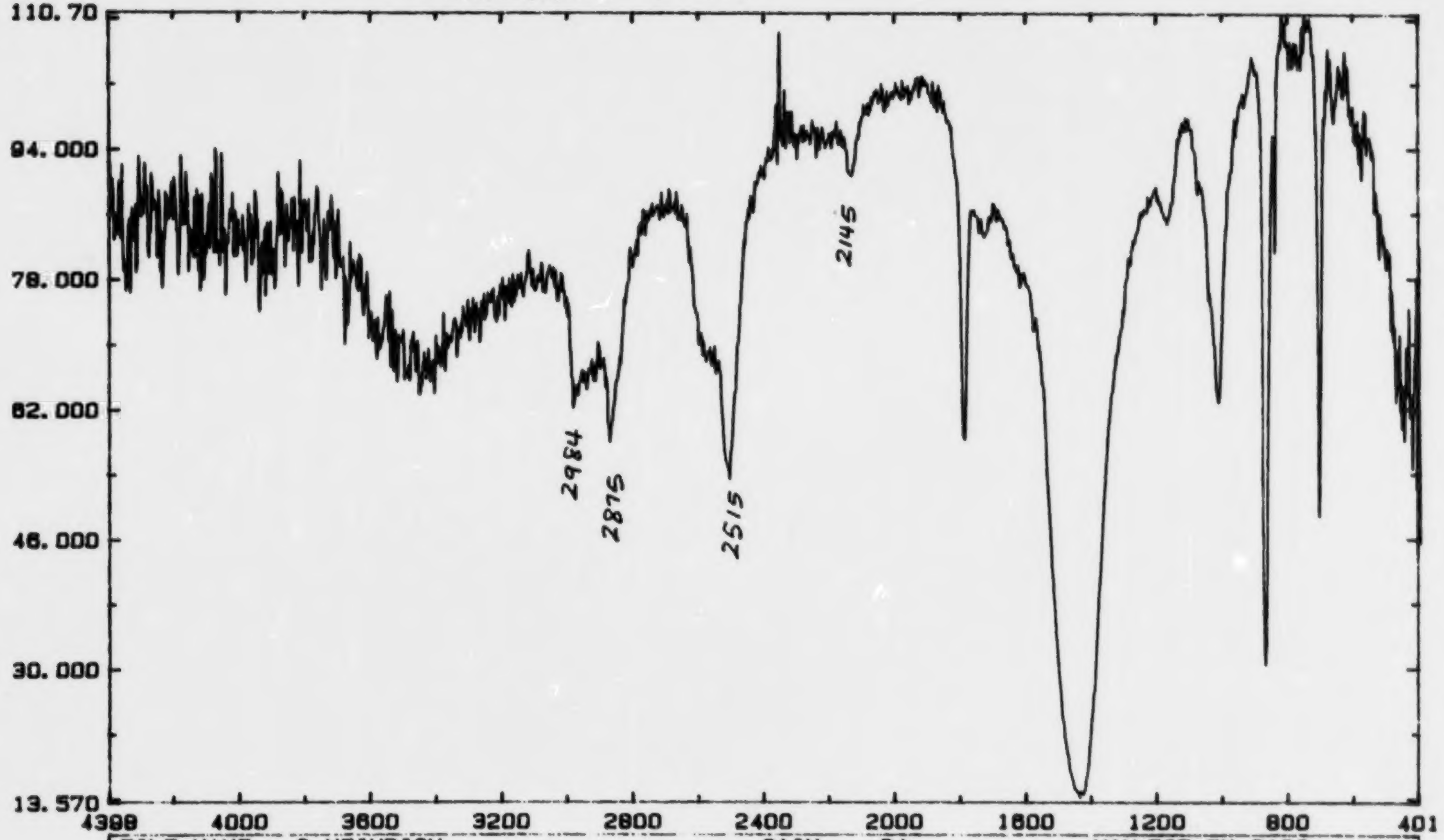


FILE NAME : G. HEINRICH
#SCANS : 300
#BKG : 64
APOD : HAPP-GENZEL
COMMENT : DRIFT SAMPLE G160: TALC/REF./COATED 1200

GAIN : 64
DET : TGS
RES : 4 CM-1
DATE :

ANALECT FX-6160
ORD : %T
ABSC: WAVENUMBER
TIME:

SPECTRUM # 5A

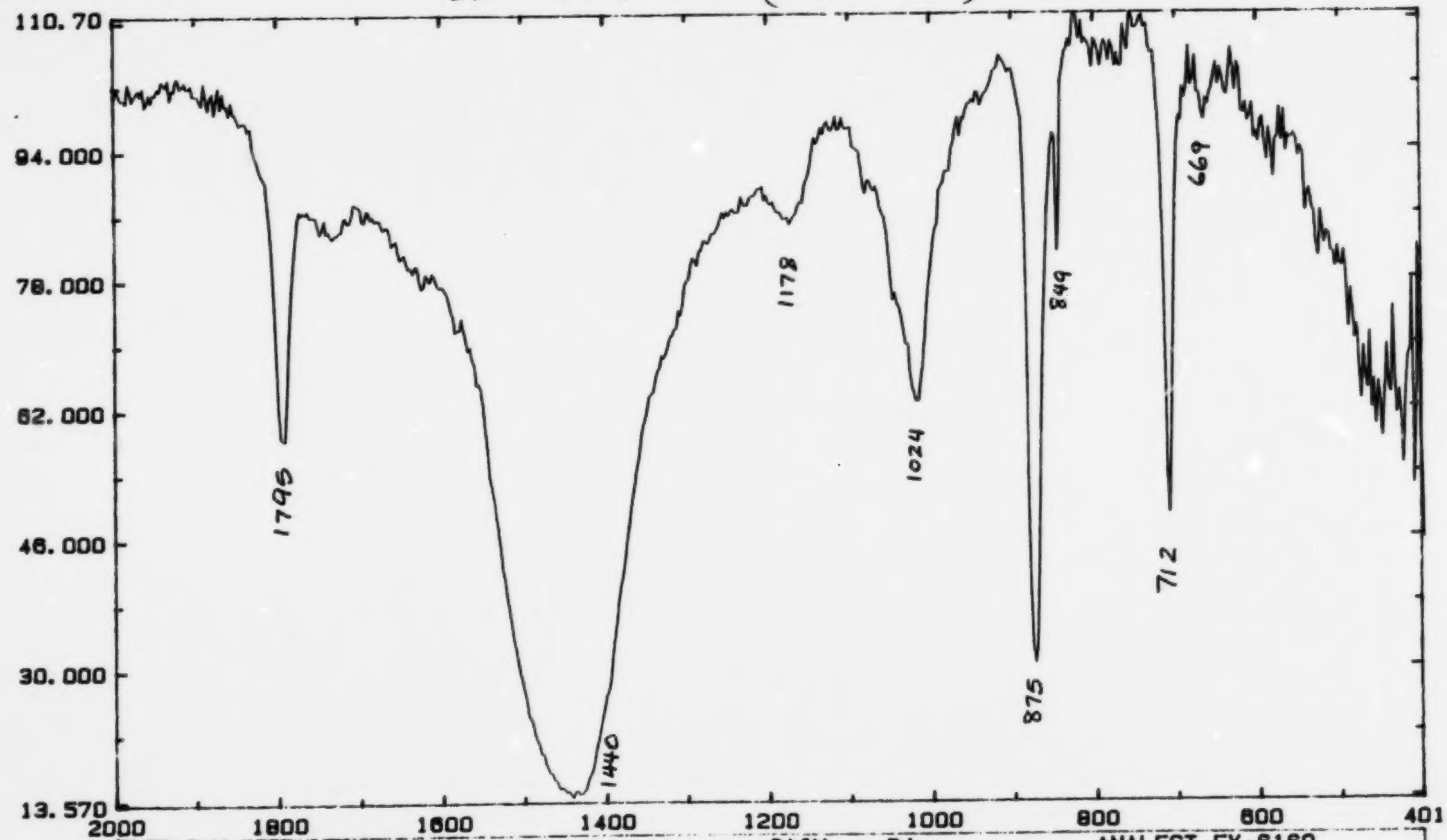


FILE NAME : G.HEINRICH
#SCANS : 300
#BKG : 64
APOD : HAPP-GENZEL
COMMENT : DRIFT SAMPLE G161: CALCITE

GAIN : 64
DET : TGS
RES : 4 CM-1
DATE :

ANALECT FX-6160
ORD : %T
ABSC: WAVENUMBER
TIME:

SPECTRUM #5A (EXPANDED)

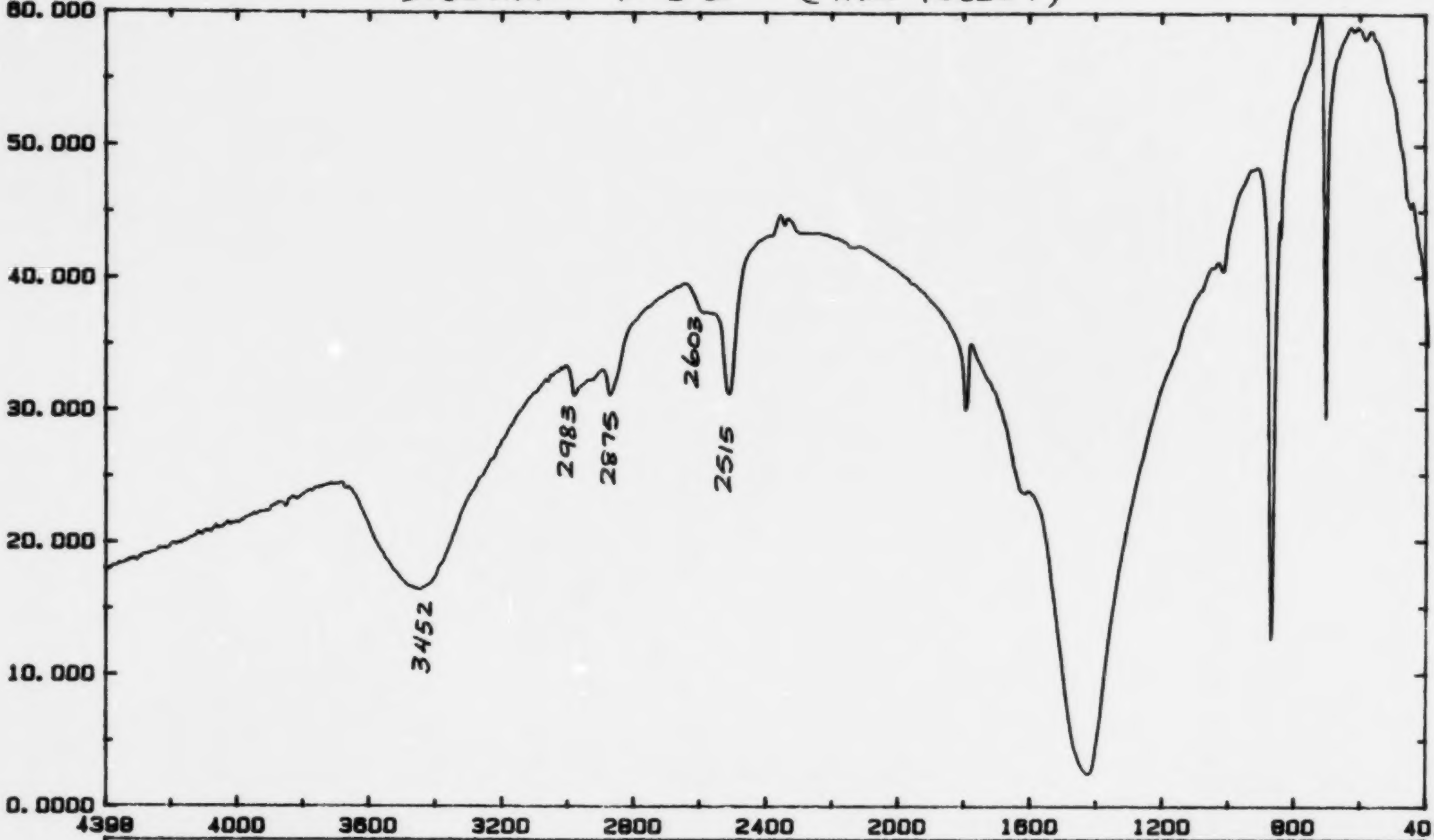


FILE NAME : G.HEINRICH
#SCANS : 300
#BKG : 64
APOD : HAPP-GENZEL
COMMENT : DRIFT SAMPLE G161:CALCITE

GAIN : 64
DET : TGS
RES : 4 CM-1
DATE :

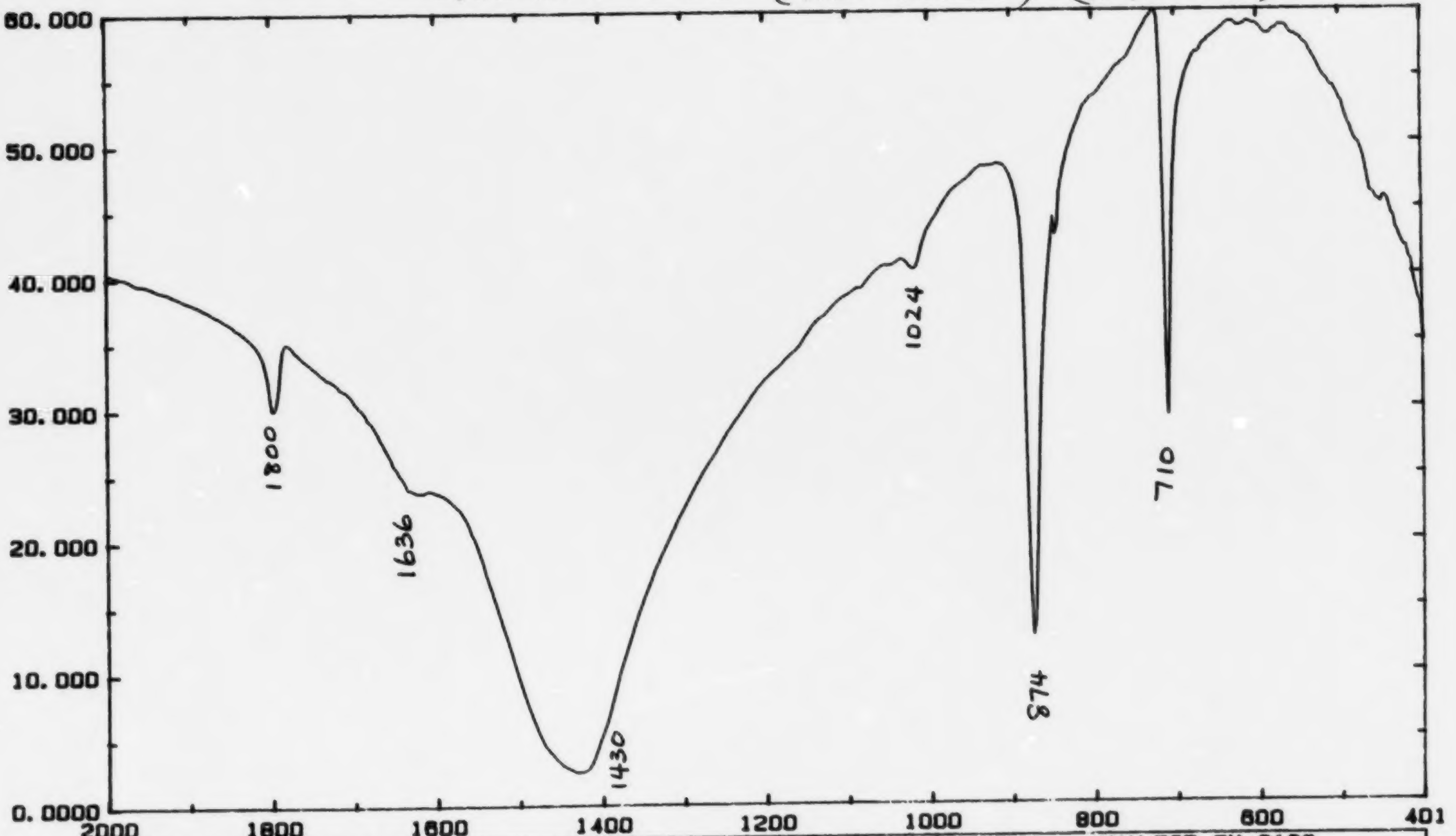
ANALECT FX-6160
ORD : %T
ABSC: WAVENUMBER
TIME:

SPECTRUM # 5B (KBR PELLET)



FILE NAME	: G. HEINRICH	GAIN	: 2	ANALECT FX-6160	
#SCANS	: 200	DET	: TGS	ORD :	%T
#BKG	: 64	RES	: 4 CM-1	ABSC:	WAVENUMBER
APOD	: HAPP-GENZEL	DATE	:	TIME:	
COMMENT	: PELLET SAMPLE G161: CALCITE				

SPECTRUM #5B (KBR PELLET) (EXPANDED)

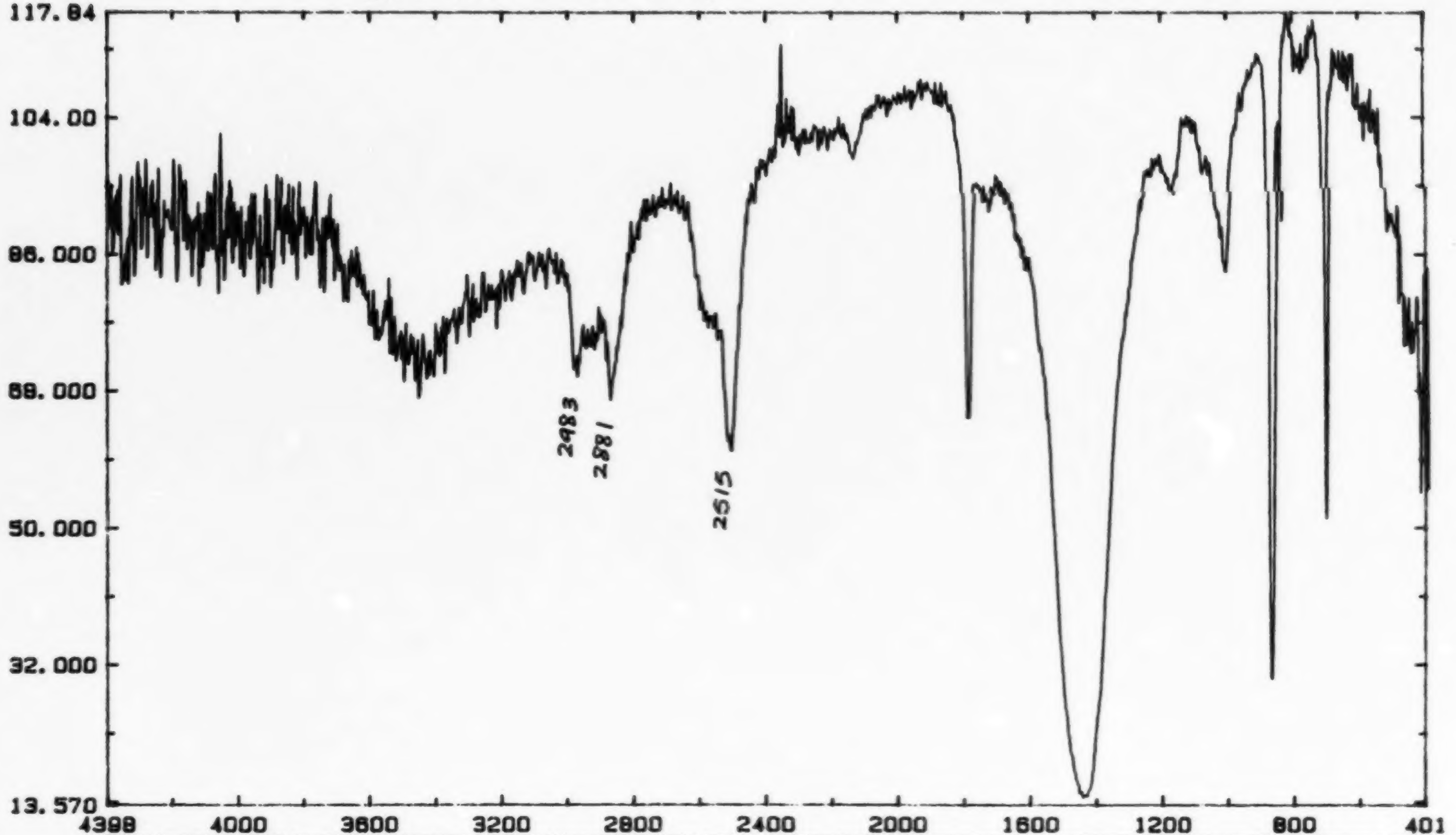


FILE NAME : G. HEINRICH
#SCANS : 200
#BKG : 64
APOD : HAPP-GENZEL
COMMENT : PELLET SAMPLE G161: CALCITE

GAIN : 2
DET : TGS
RES : 4 CM-1
DATE :

ANALECT FX-6160
ORD : %T
ABSC: WAVENUMBER
TIME:

SPECTRUM # 6A

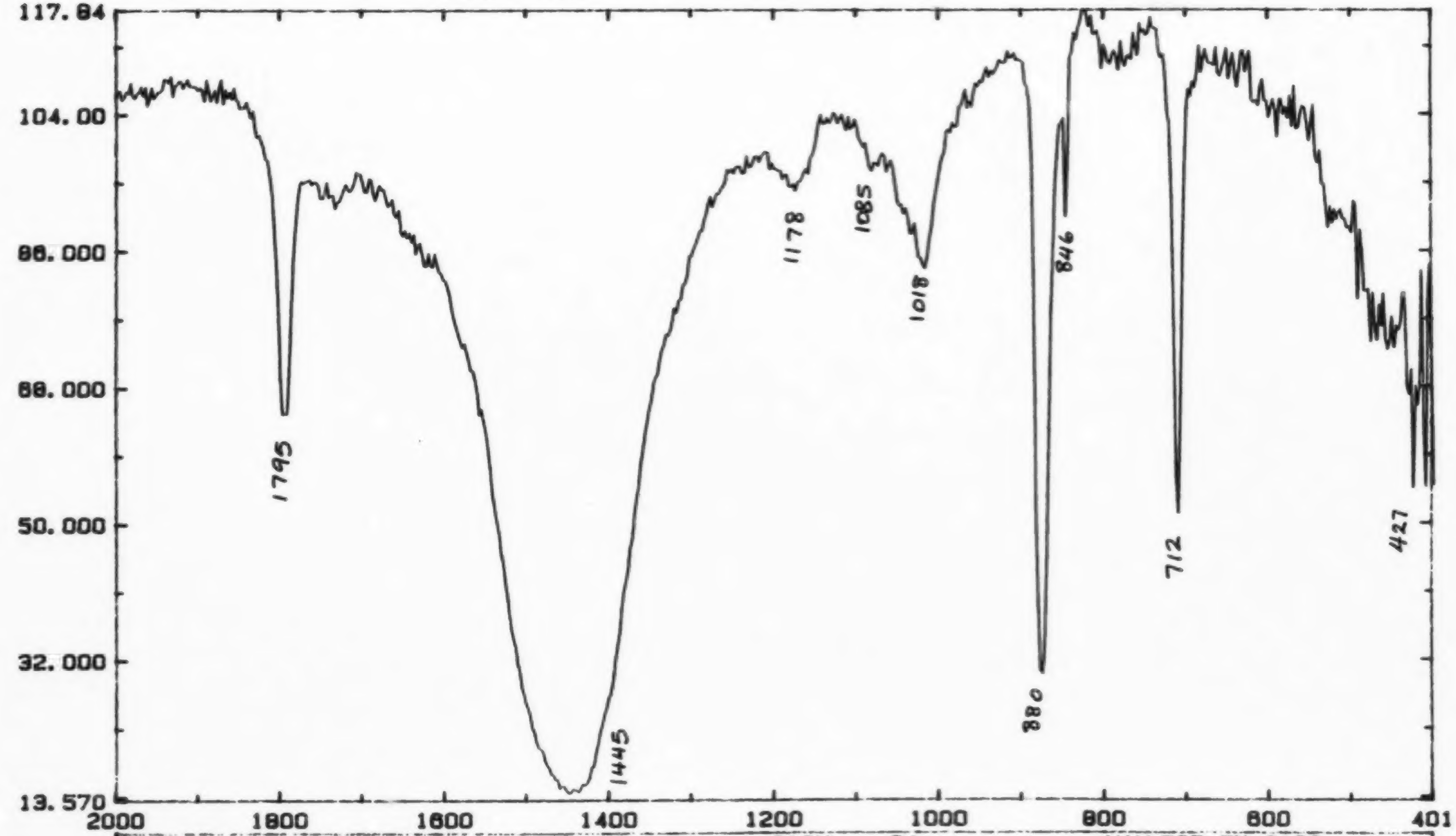


FILE NAME : G. HEINRICH
#SCANS : 300
#BKG : 64
APOD : HAPP-GENZEL
COMMENT : DRIFT SAMPLE G162: CALCITE/COATED

GAIN : 64
DET : TGS
RES : 4 CM-1
DATE :

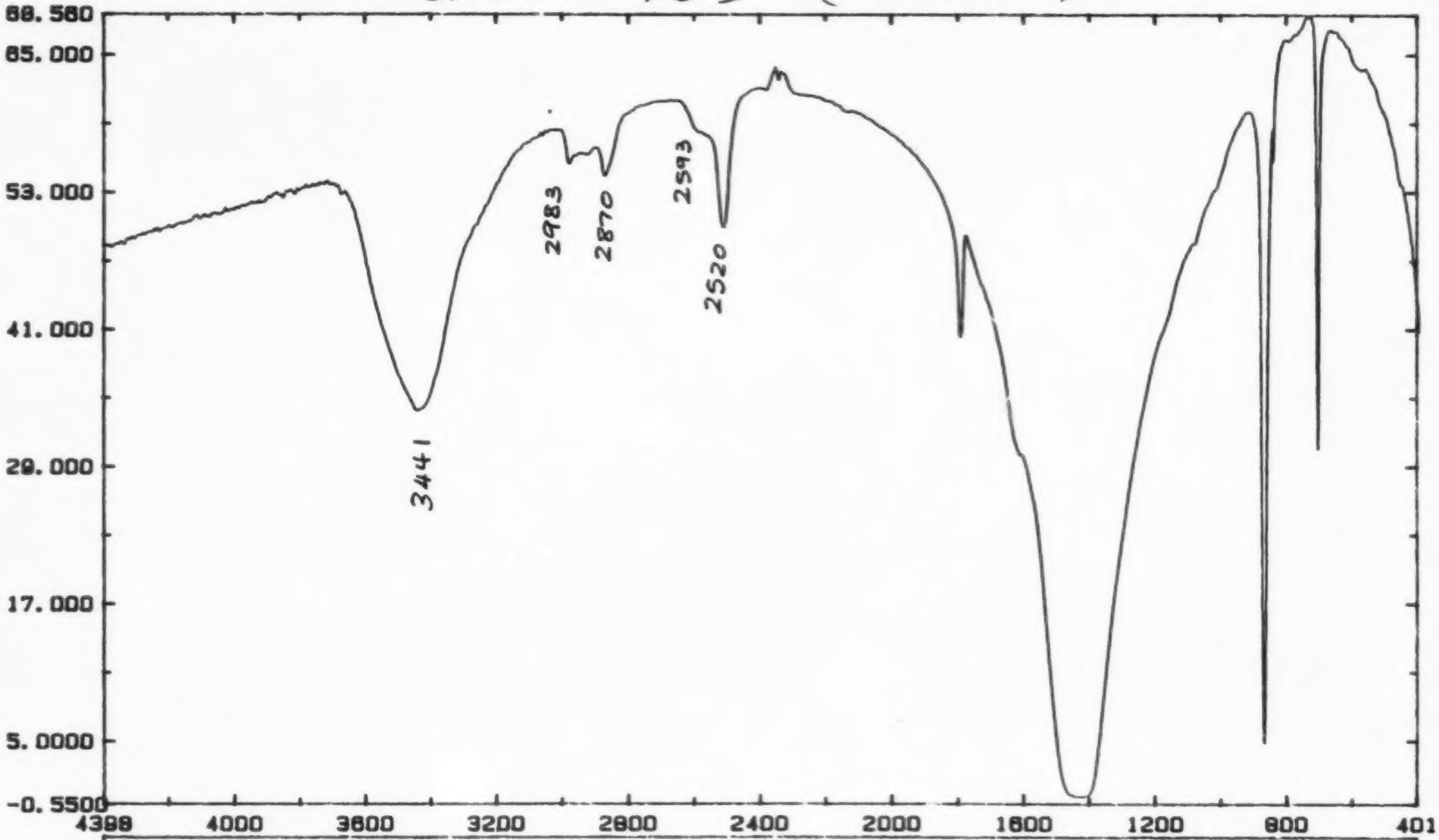
ANALECT FX-6160
ORD : %T
ABSC: WAVENUMBER
TIME:

SPECTRUM #6 A (EXPANDED)



FILE NAME	: G. HEINRICH	GAIN	: 64	ANALECT FX-6160	
#SCANS	: 300	DET	: TGS	ORD	: %T
#BKG	: 64	RES	: 4 CM-1	ABSC:	WAVENUMBER
APOD	: HAPP-GENZEL	DATE	:	TIME:	
COMMENT	: DRIFT SAMPLE G162: CALCITE/COATED				

SPECTRUM #6 B (KBr. PELLET)

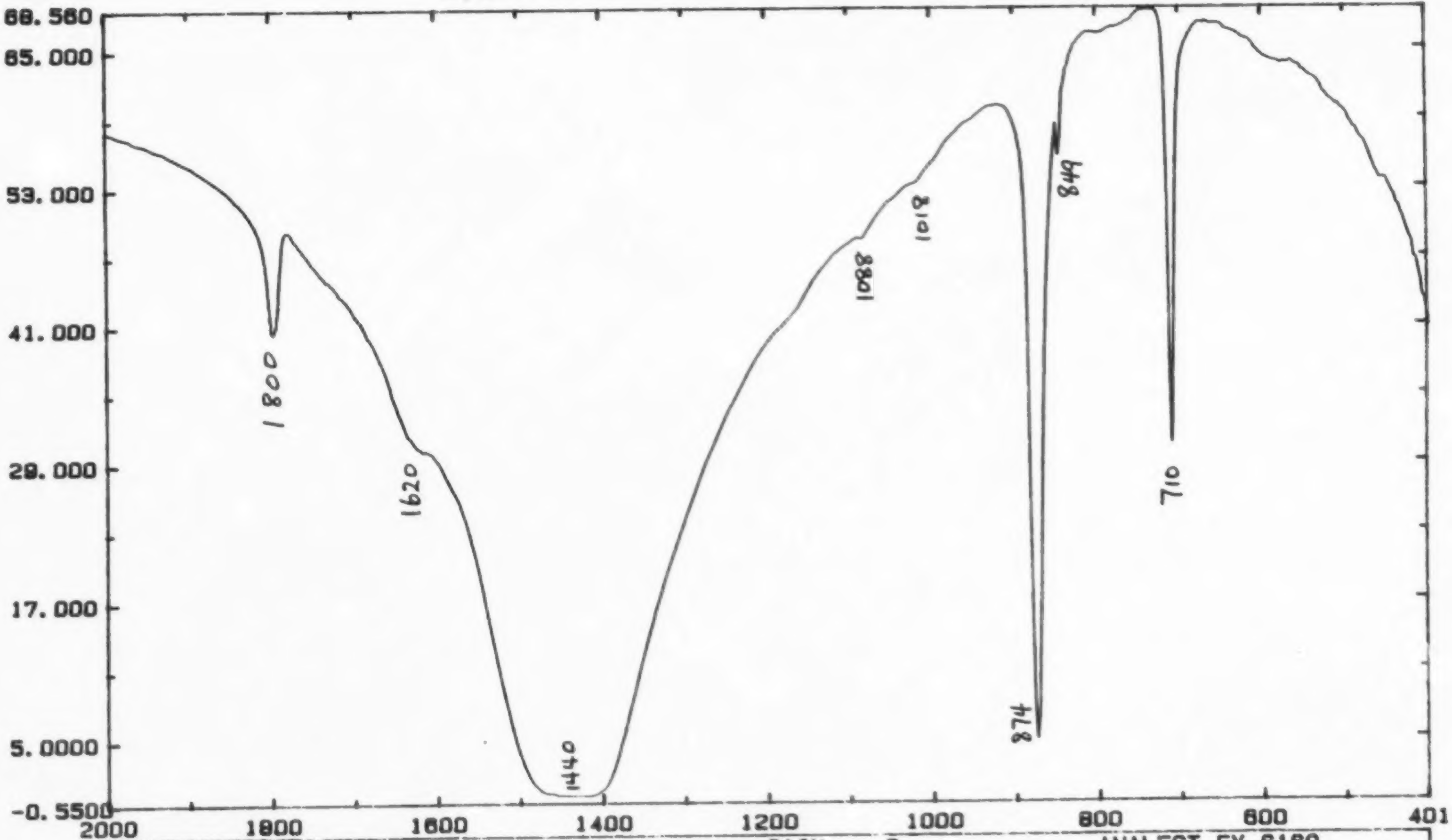


FILE NAME : G. HEINRICH
#SCANS : 200
#BKG : 64
APOD : HAPP-GENZEL
COMMENT : PELLET SAMPLE G162: CALCITE/COATED

GAIN : 2
DET : TGS
RES : 4 CM-1
DATE :

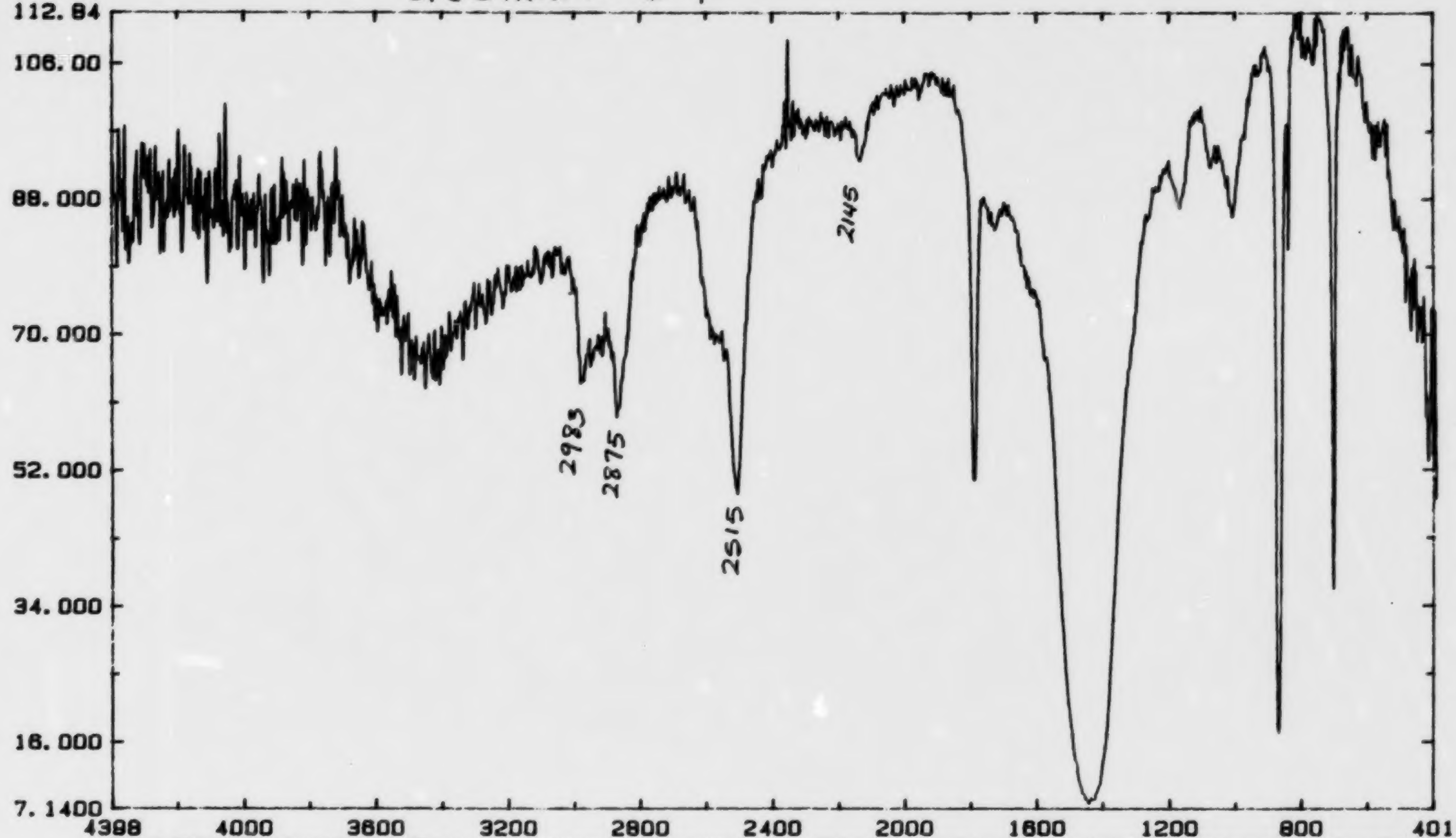
ANALECT FX-6160
ORD : %T
ABSC: WAVENUMBER
TIME:

SPECTRUM #6 B (KBR PELLET) (EXPANDED)



FILE NAME : G. HEINRICH
#SCANS : 200
#BKG : 64
APOD : HAPP-GENZEL
COMMENT : PELLET SAMPLE G162: CALCITE/COATED
GAIN : 2
DET : TGS
RES : 4 CM-1
DATE :
ANALECT FX-6160
ORD : %T
ABSC: WAVENUMBER
TIME:

SPECTRUM #7

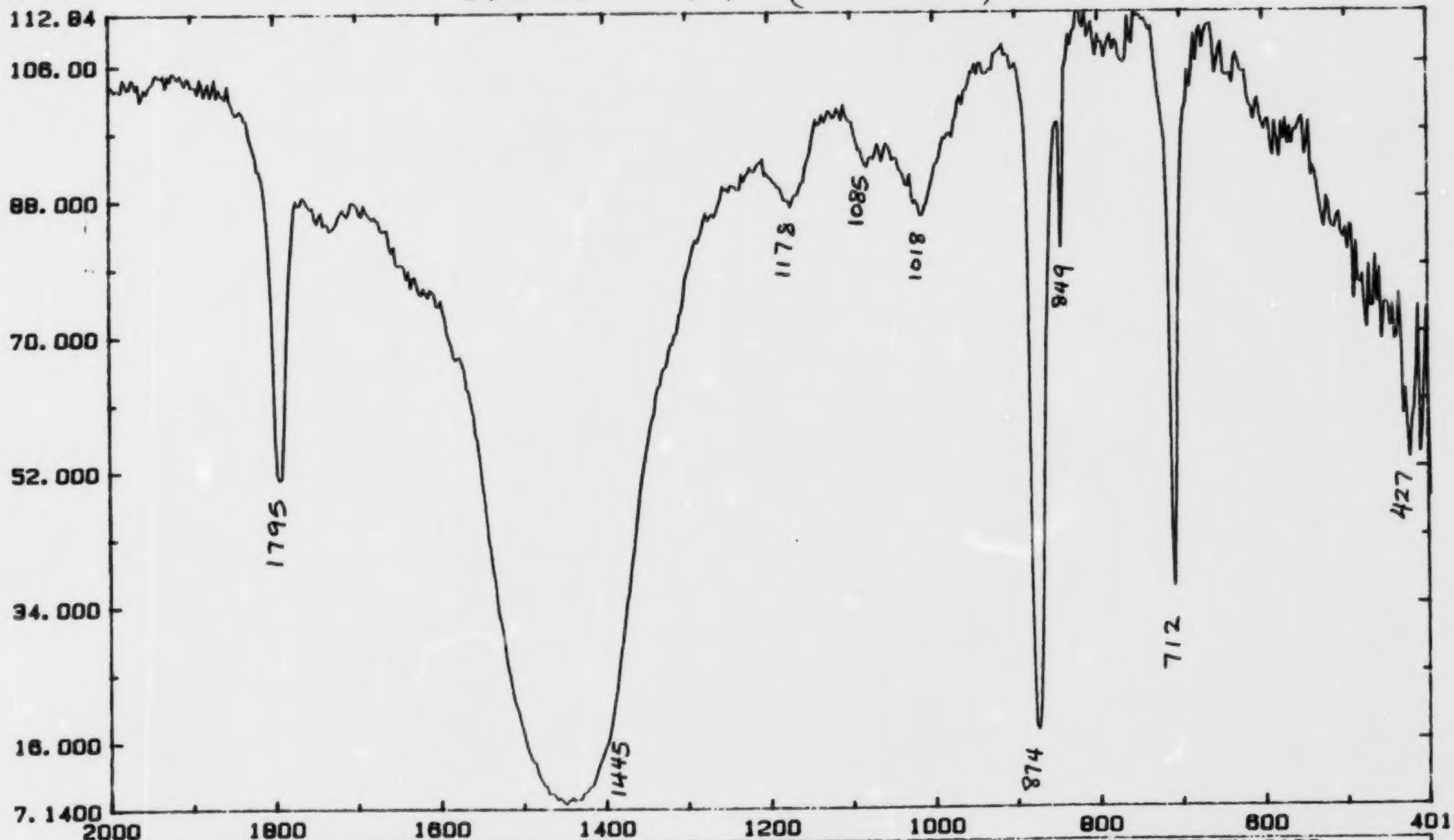


FILE NAME : G.HEINRICH
#SCANS : 300
#BKG : 64
APOD : HAPP-GENZEL
COMMENT : DRIFT SAMPLE G163; CALCITE/REF. /-15-15

GAIN : 64
DET : TGS
RES : 4 CM-1
DATE :

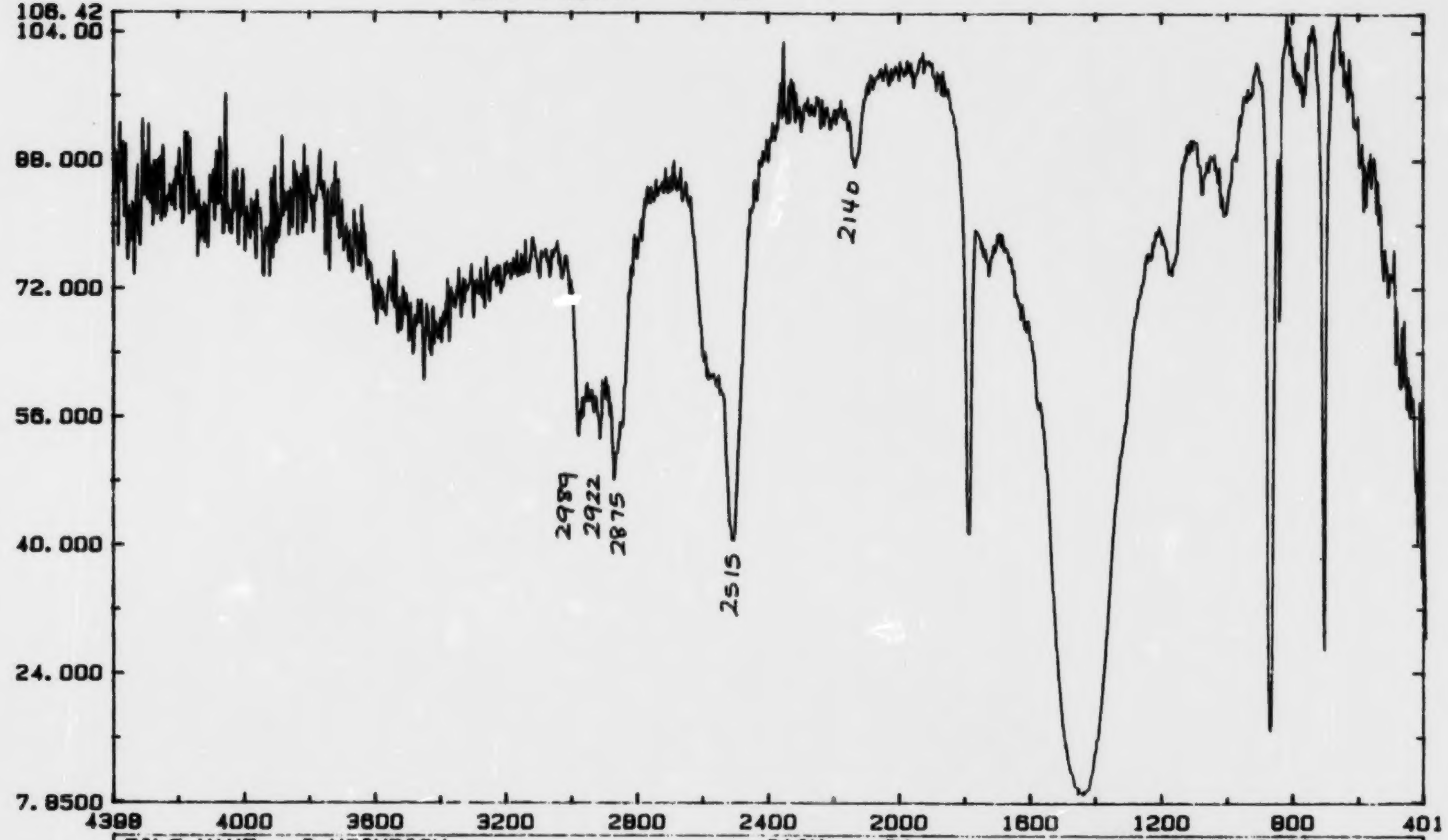
ANALECT FX-6160
ORD : %T
ABSC: WAVENUMBER
TIME:

SPECTRUM #7 (EXPANDED)



FILE NAME	: G. HEINRICH	GAIN	: 64	ANALECT FX-6160	
#SCANS	: 300	DET	: TGS	ORD	: %T
#BKG	: 64	RES	: 4 CM-1	ABSC	: WAVENUMBER
APOD	: HAPP-GENZEL	DATE	:	TIME	:
COMMENT	: DRIFT SAMPLE G163: CALCITE/REF. /-15-15				

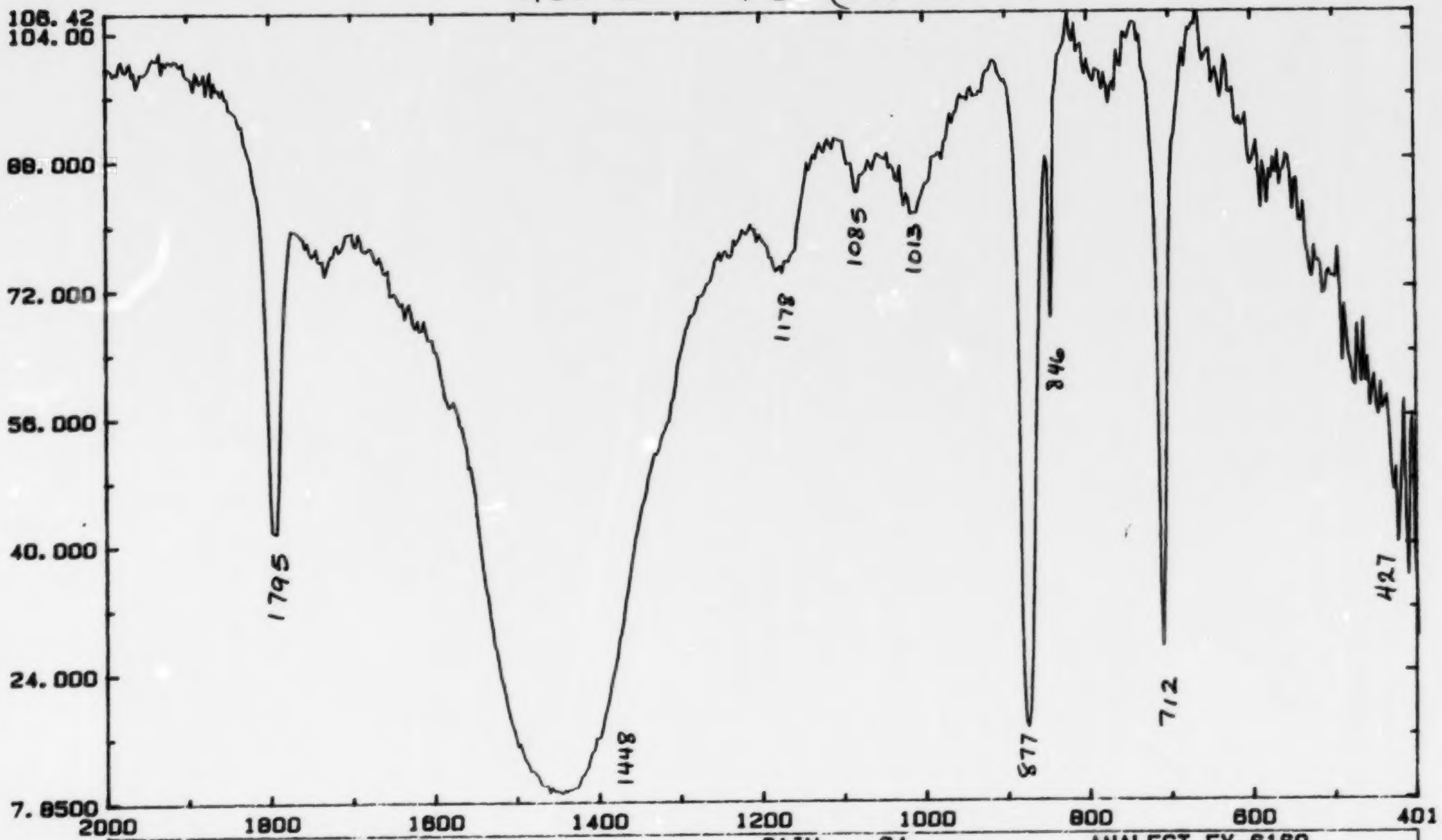
SPECTRUM #8



FILE NAME	: G.HEINRICH	GAIN	: 64	ANALECT FX-6160
#SCANS	: 300	DET	: TGS	ORD : %T
#BKG	: 64	RES	: 4 CM-1	ABSC: WAVENUMBER
APOD	: HAPP-GENZEL	DATE	:	TIME:

COMMENT : DRIFT SAMPLE G164: CALCITE/REF/COATED 402

SPECTRUM #8 (EXPANDED)

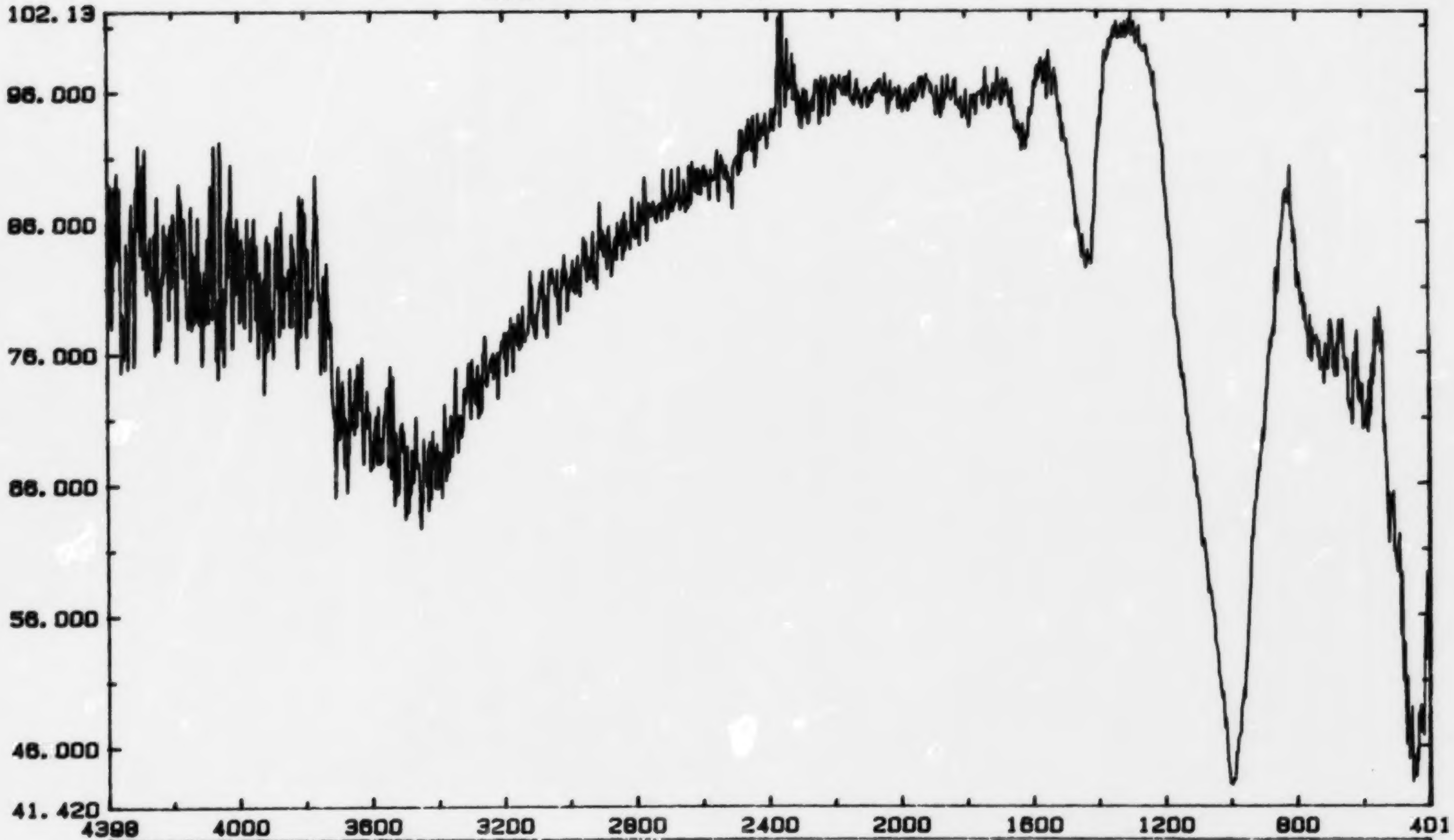


FILE NAME : G. HEINRICH
#SCANS : 300
#BKG : 64
APOD : HAPP-GENZEL
COMMENT : DRIFT SAMPLE G164: CALCITE/REF/COATED 402

GAIN : 64
DET : TGS
RES : 4 CM-1
DATE :

ANALECT FX-6160
ORD : %T
ABSC: WAVENUMBER
TIME:

SPECTRUM #9

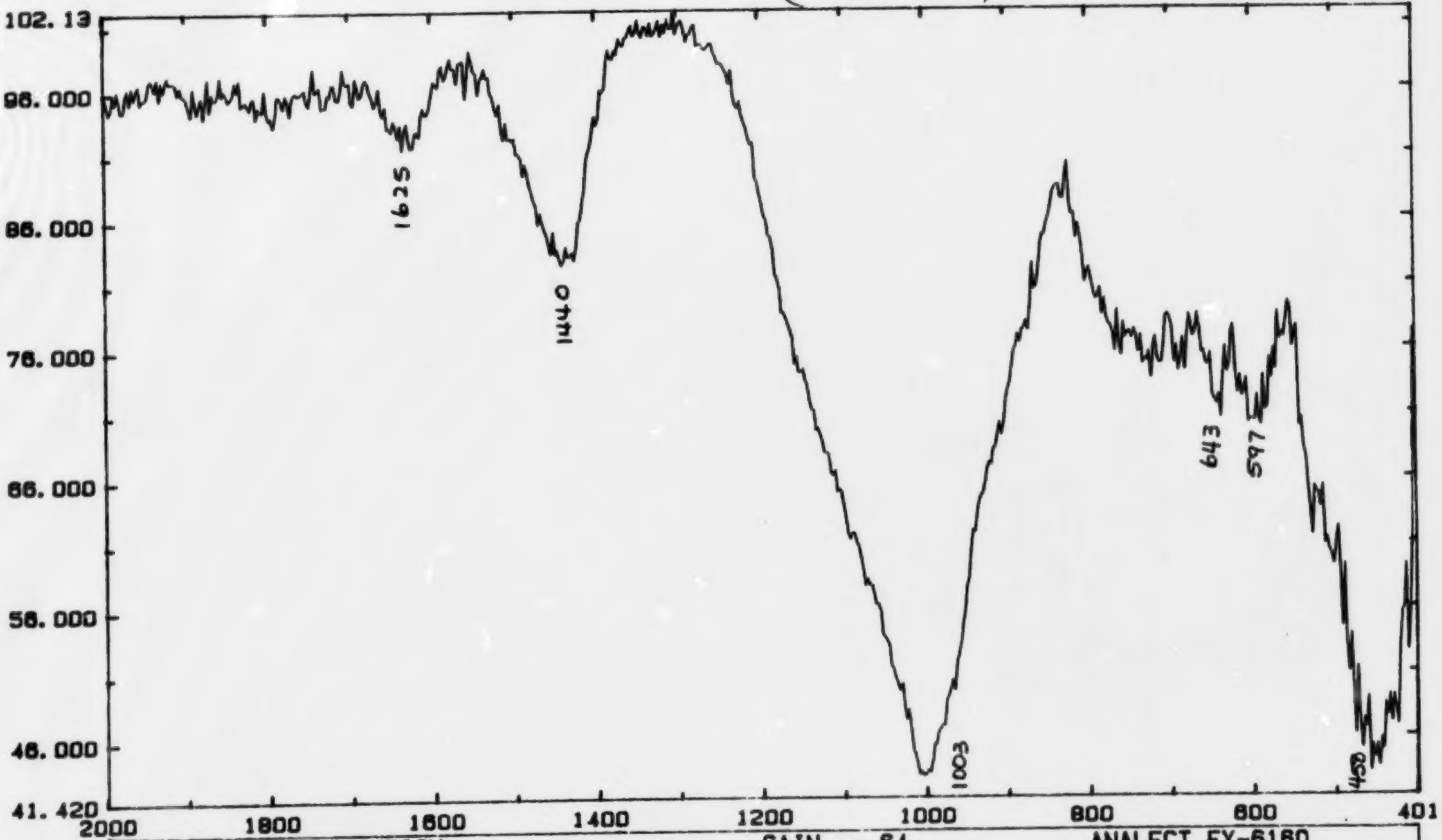


FILE NAME : G.HEINRICH
#SCANS : 300
#BKG : 64
APOD : HAPP-GENZEL
COMMENT : DRIFT SAMPLE G165: SAZORITE

GAIN : 64
DET : TGS
RES : 4 CM-1
DATE :

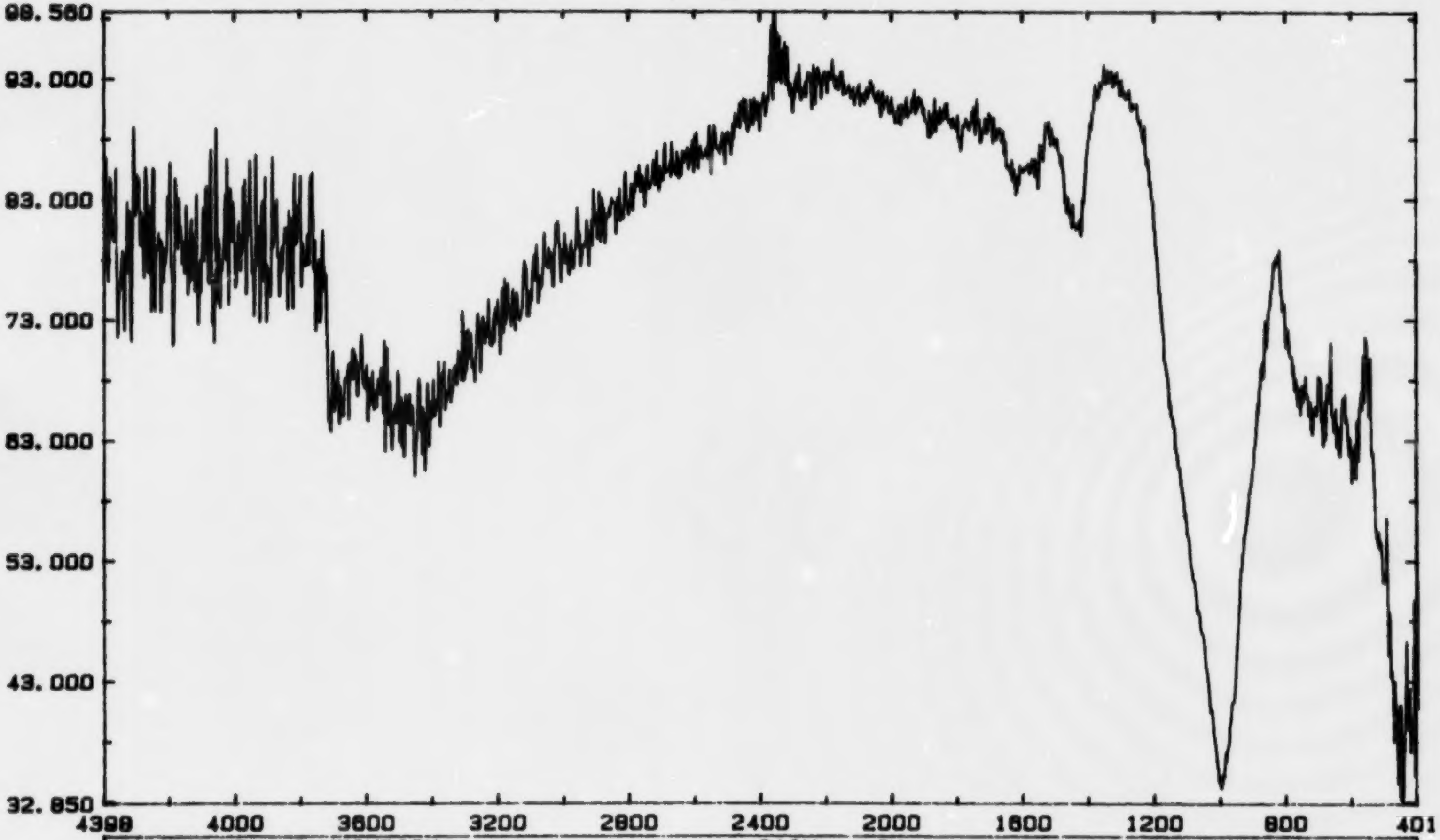
ANALECT FX-6160
ORD : %T
ABSC: WAVENUMBER
TIME:

SPECTRUM #9 (EXPANDED)



FILE NAME	: G. HEINRICH	GAIN	: 64	ANALECT FX-6160	
#SCANS	: 300	DET	: TGS	ORD :	%T
#BKG	: 64	RES	: 4 CM-1	ABSC:	WAVENUMBER
APOD	: HAPP-GENZEL	DATE	:	TIME:	
COMMENT	: DRIFT SAMPLE G165: SAZORITE				

SPECTRUM # 10

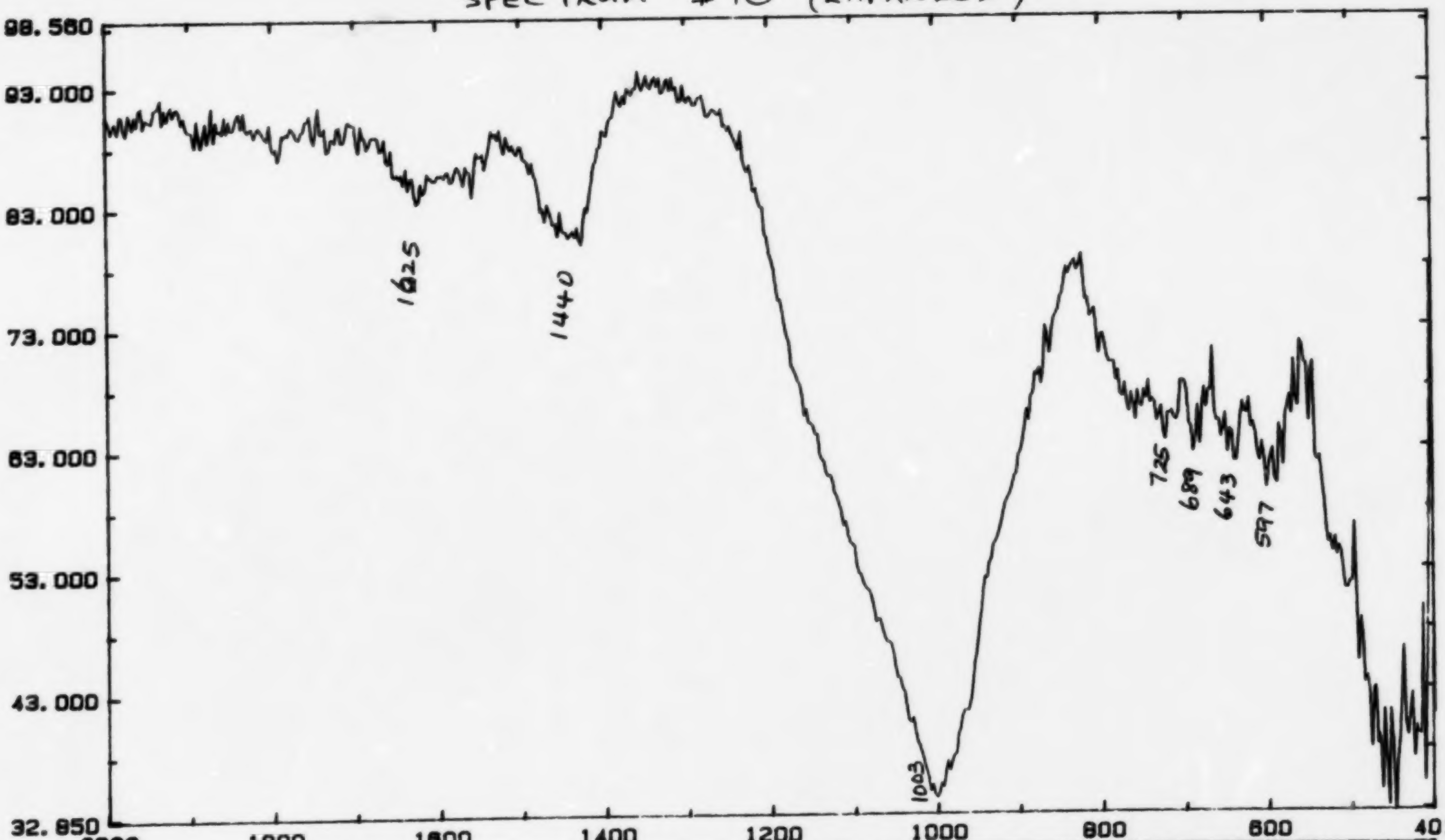


FILE NAME : G.HEINRICH
#SCANS : 300
#BKG : 64
APOD : HAPP-GENZEL
COMMENT : DRIFT SAMPLE G166: SAZORITE/COATED

GAIN : 64
DET : TGS
RES : 4 CM-1
DATE :

ANALECT FX-6160
ORD : %T
ABSC: WAVENUMBER
TIME:

SPECTRUM #10 (EXPANDED)

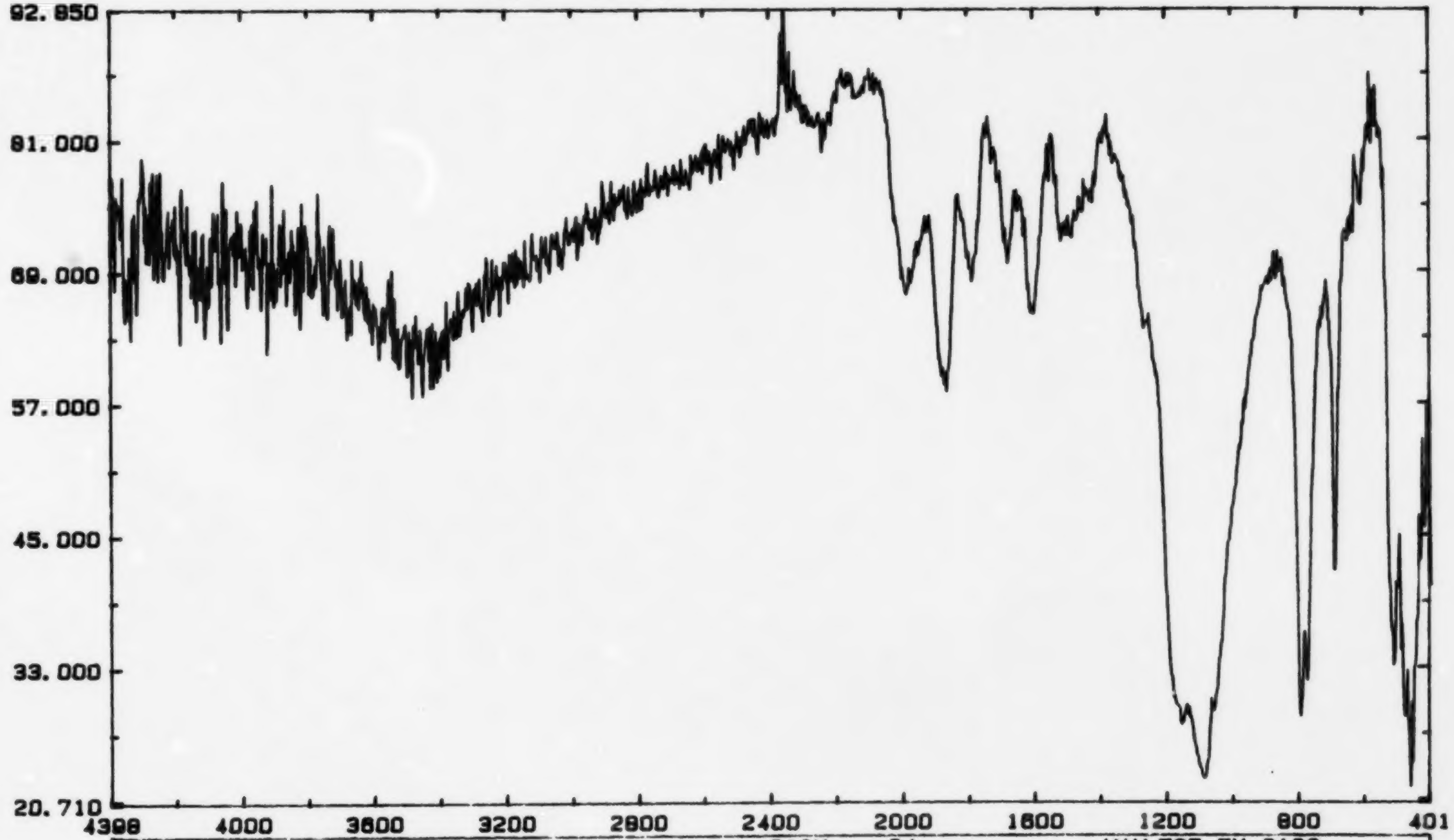


FILE NAME : G. HEINRICH
#SCANS : 300
#BKG : 64
APOD : HAPP-GENZEL
COMMENT : DRIFT SAMPLE G166: SAZORITE/COATED

GAIN : 64
DET : TGS
RES : 4 CM-1
DATE :

ANALECT FX-6160
ORD : %T
ABSC: WAVENUMBER
TIME:

SPECTRUM # 11

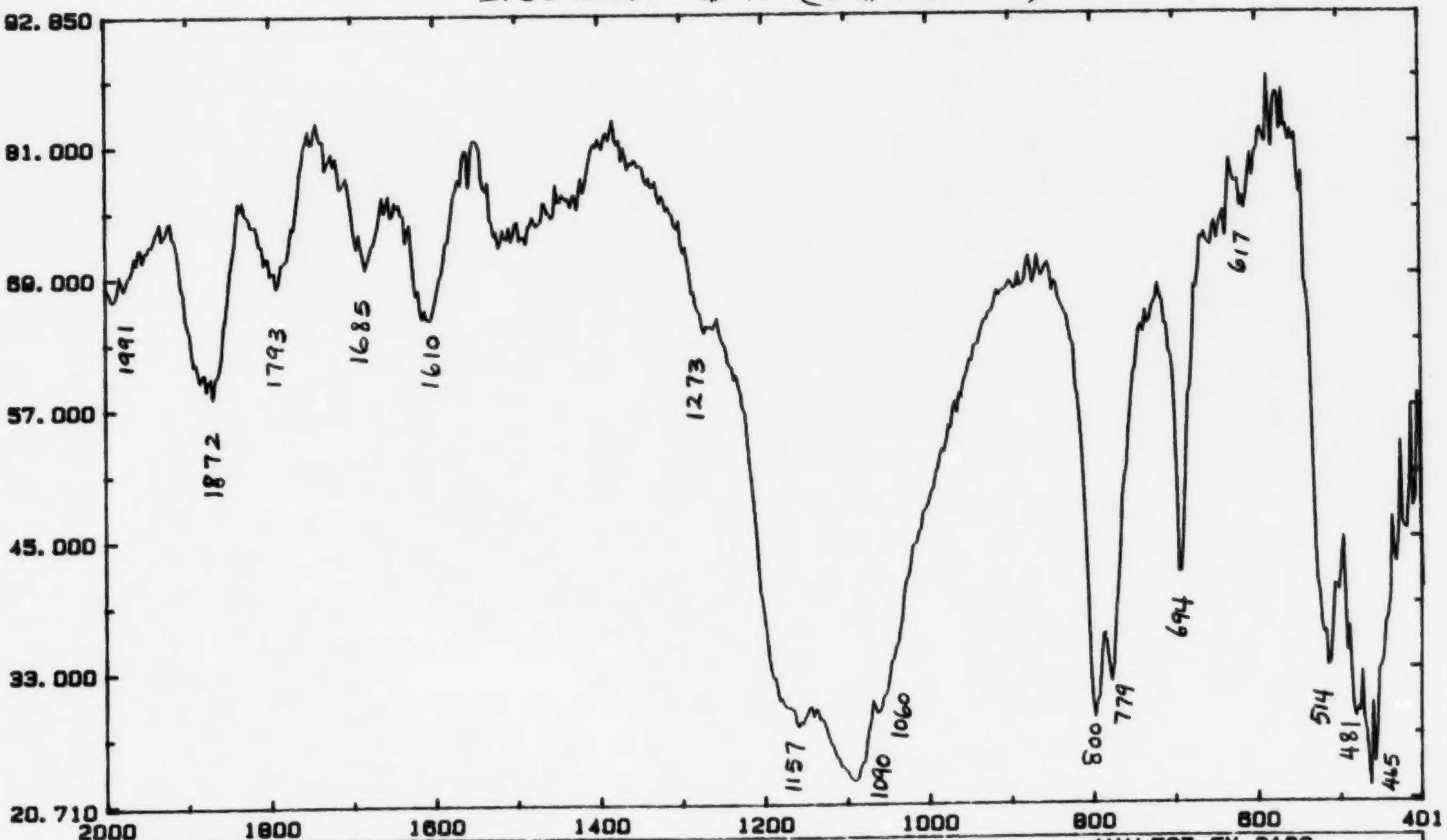


FILE NAME : G.HEINRICH
#SCANS : 300
#BKG : 64
APOD : HAPP-GENZEL
COMMENT : DRIFT SAMPLE G167: S102

GAIN : 64
DET : TGS
RES : 4 CM-1
DATE :

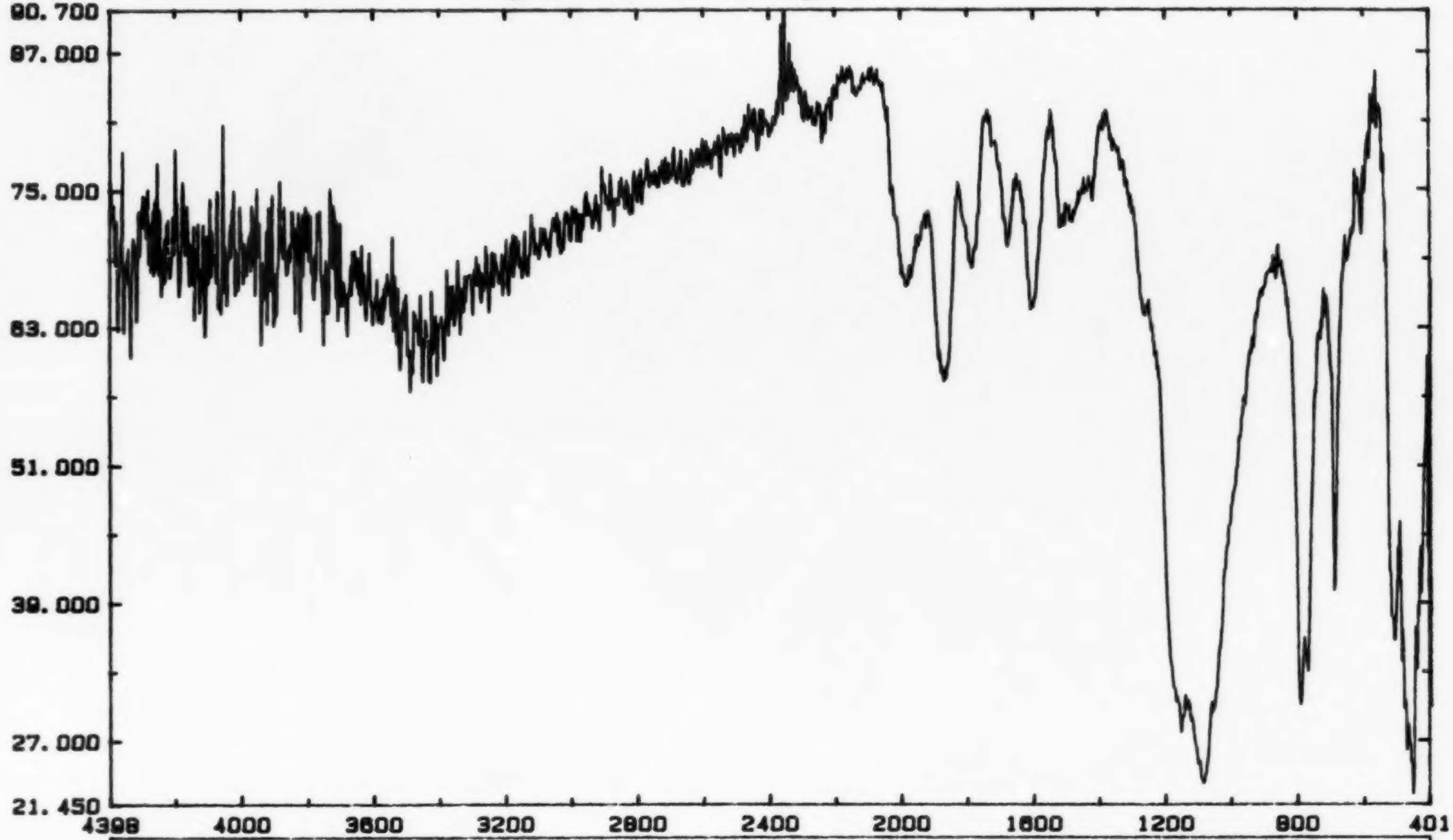
ANALECT FX-6160
ORD : %T
ABSC: WAVENUMBER
TIME:

SPECTRUM # 11 (EXPANDED)



FILE NAME	: G. HEINRICH	GAIN	: 64	ANALECT FX-6160		
#SCANS	: 300	DET	: TGS	ORD : %T		
#BKG	: 64	RES	: 4 CM-1	ABSC: WAVENUMBER		
APOD	: HAPP-GENZEL	DATE	:	TIME:		
COMMENT	: DRIFT SAMPLE G167: S102					

SPECTRUM # 12

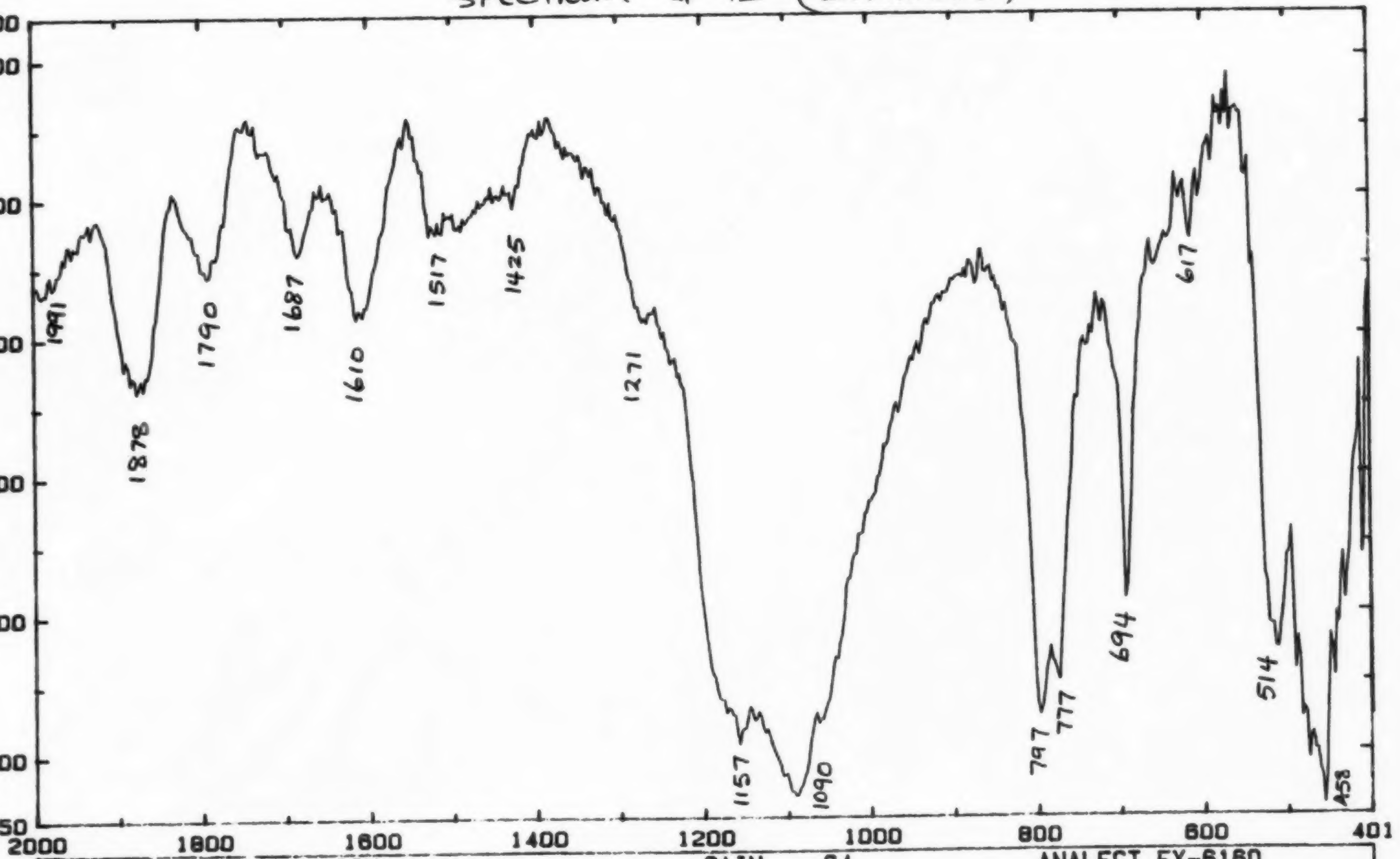


FILE NAME : G. HEINRICH
#SCANS : 300
#BKG : 64
APOD : HAPP-GENZEL
COMMENT : DRIFT SAMPLE G168: SiO2/COATED

GAIN : 64
DET : TGS
RES : 4 CM-1
DATE :

ANALECT FX-6160
ORD : %T
ABSC: WAVENUMBER
TIME:

SPECTRUM # 12 (EXPANDED)



FILE NAME : G.HEINRICH
#SCANS : 300
#BKG : 64
APOD : HAPP-GENZEL
COMMENT : DRIFT SAMPLE G168: SiO2/COATED

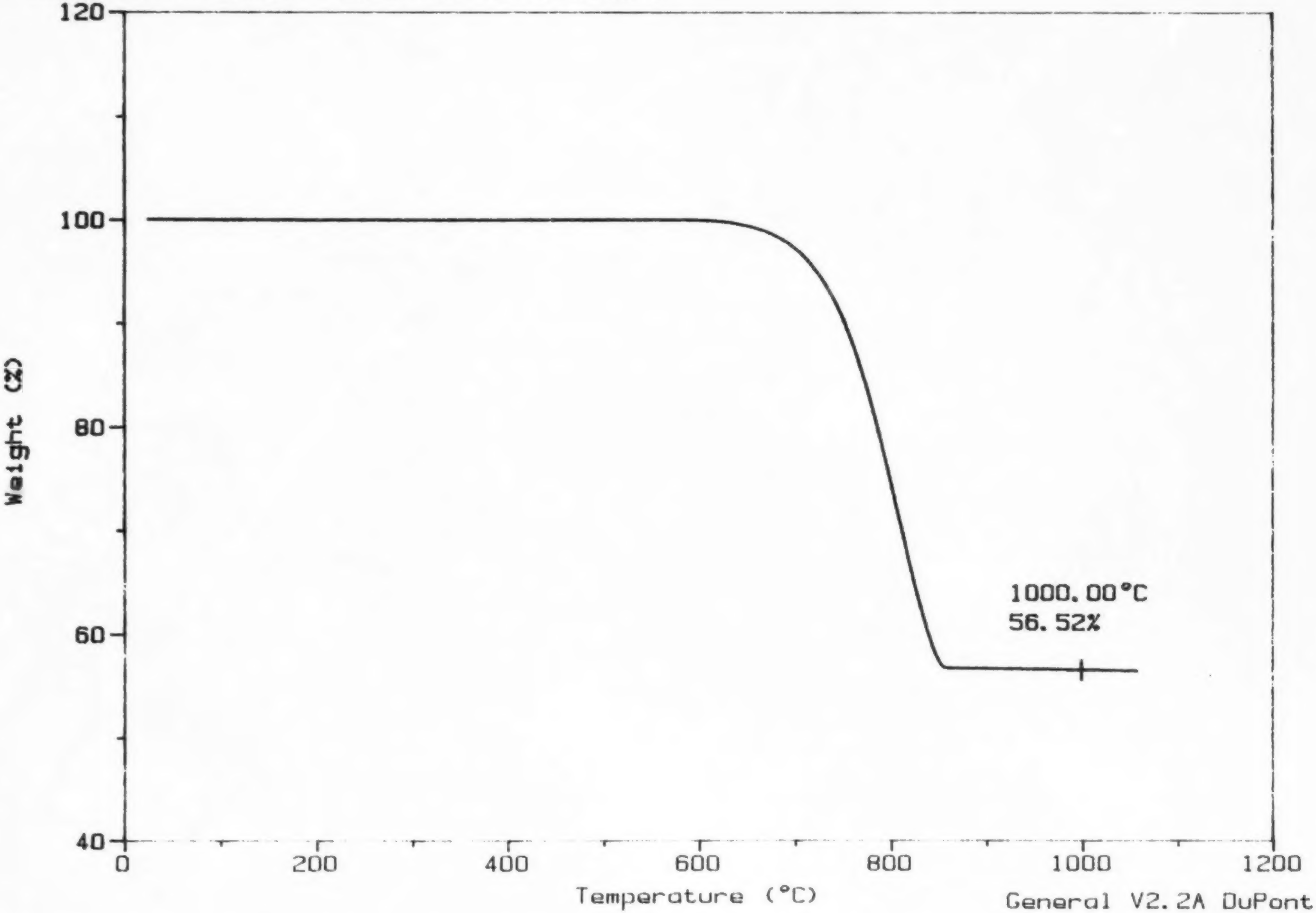
GAIN : 64
DET : TGS
RES : 4 CM-1
DATE :

ANALECT FX-6160
ORD : %T
ABSC: WAVENUMBER
TIME:

Sample: G163 CALCITE/REF/15-15 16/3/88
Size: 50.9470 mg
Method: TGA-HIGHT TEMP
Comment: 10°C/MIN. 100CC/MIN N2 TO 1000°C

TGA #1
(FULL SCALE)

File: PILOT.01
Operator: L.CHU
Run Date: 03/26/88 09:26

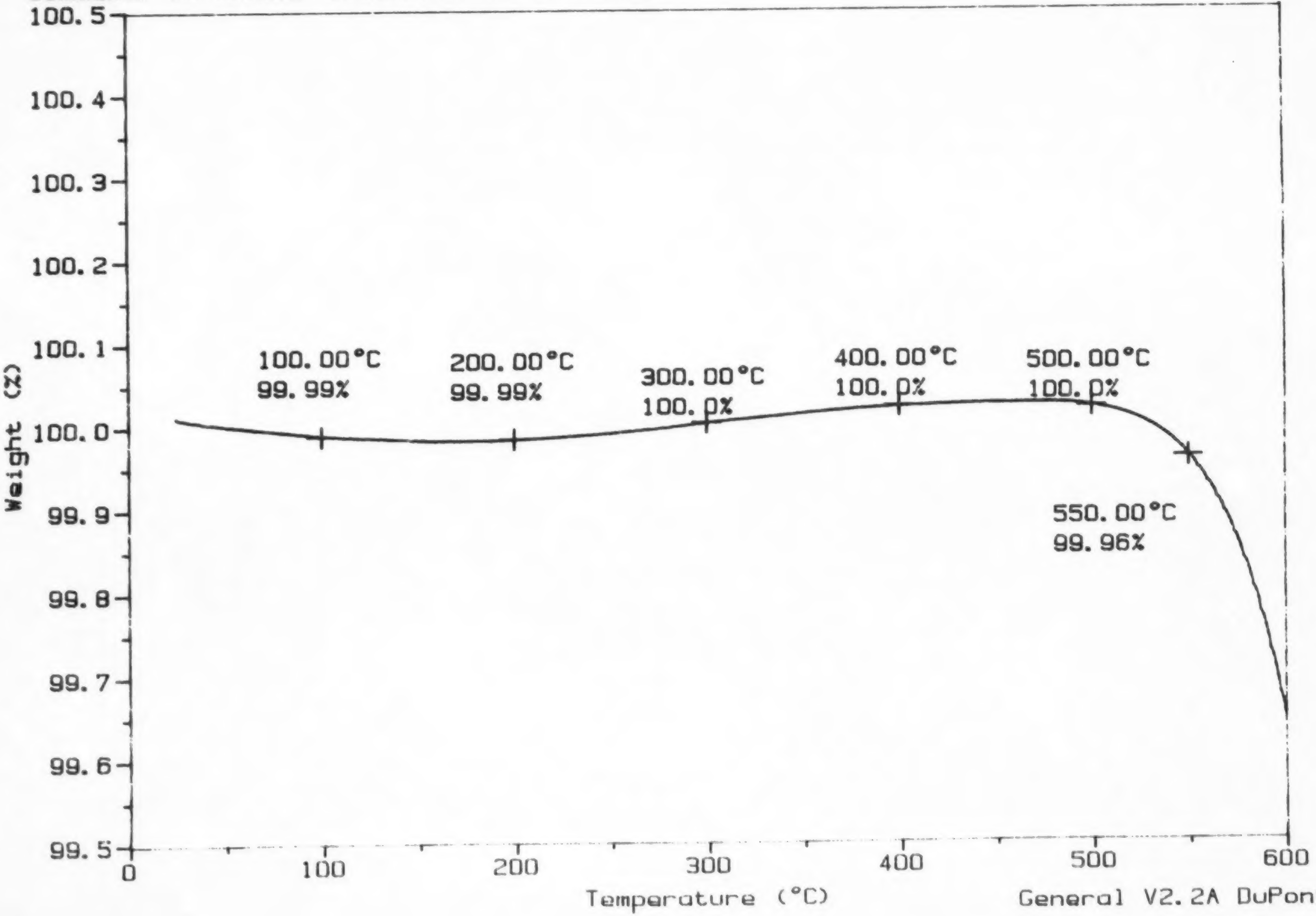


General V2.2A DuPont 9900

Sample: G163 CALCITE/REF/15-15 16/3/88
Size: 50.9470 mg
Method: TGA-HIGHT TEMP
Comment: 10°C/MIN. 100CC/MIN N2 TO 1000°C

TGA #1
(EXPANDED)

File: PILOT.01
Operator: L.CHU
Run Date: 03/26/88 09:26

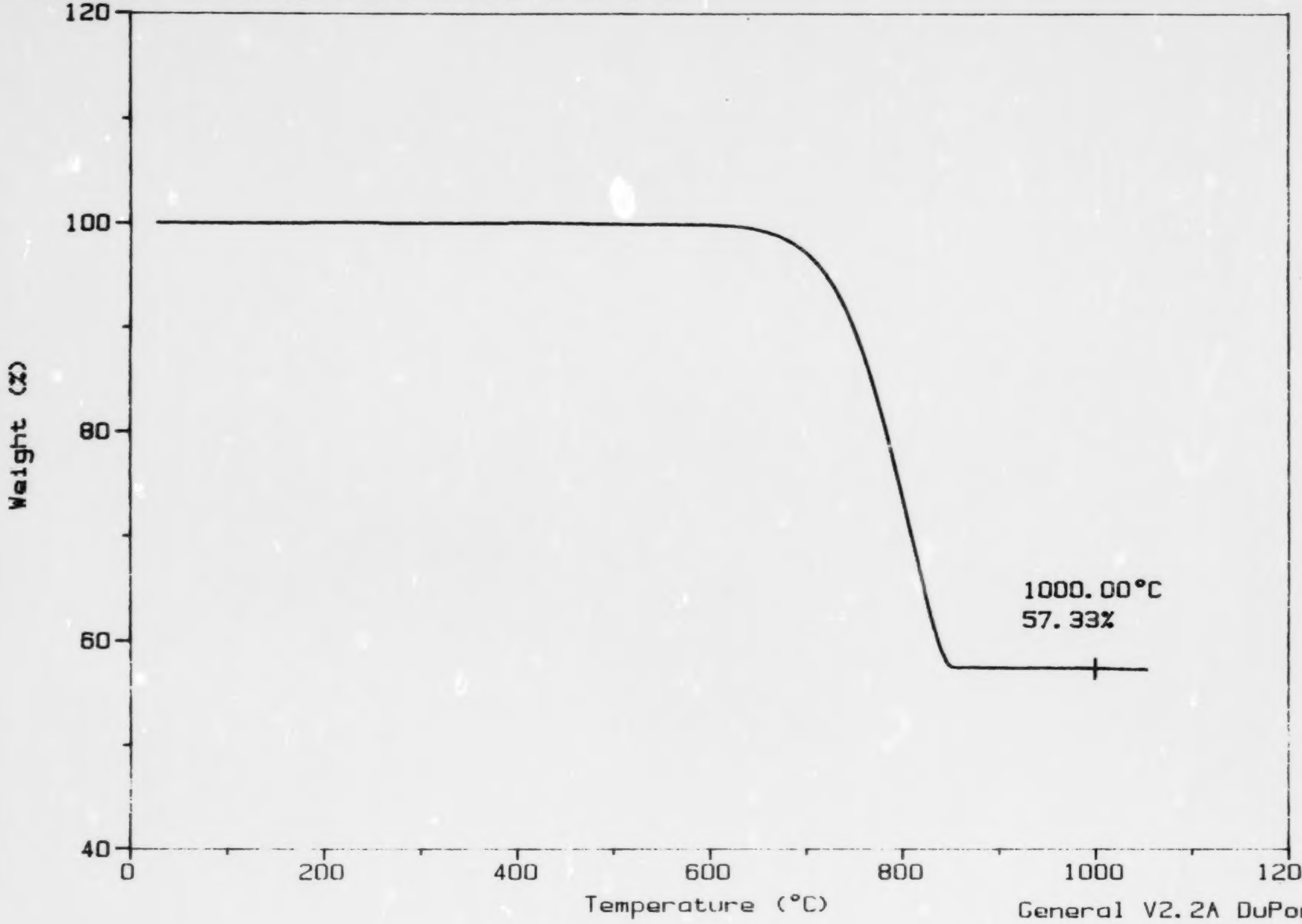


General V2.2A DuPont 9900

Sample: G164 CALCITE/REF/COATED 4 02
Size: 50.9590 mg
Method: TGA-HIGHT TEMP
Comment: 10°C/MIN, 100CC/MIN N2 TO 1000°C

TGA #2
(FULL SCALE)

File: PILOT.02
Operator: L.CHU
Run Date: 03/26/88 13:34

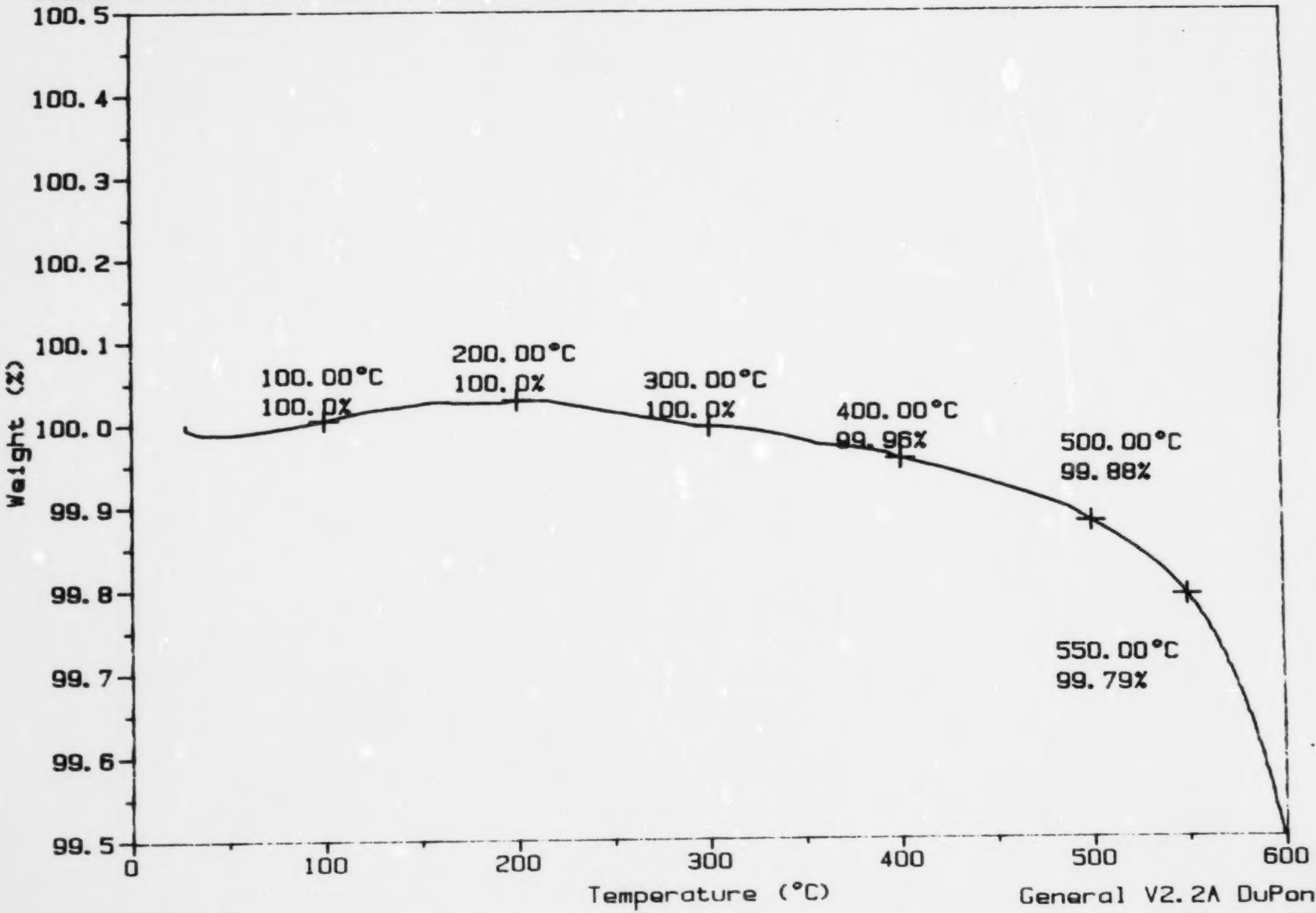


General V2.2A DuPont 9900

Sample: G164 CALCITE/REF/COATED 4 02
Size: 50.9590 mg
Method: TGA-HIGHT TEMP
Comment: 10°C/MIN. 100CC/MIN N2 TO 1000°C

TGA #2
(EXPANDED)

File: PILOT.02
Operator: L.CHU
Run Date: 03/26/88 13:34



General V2.2A DuPont 990C